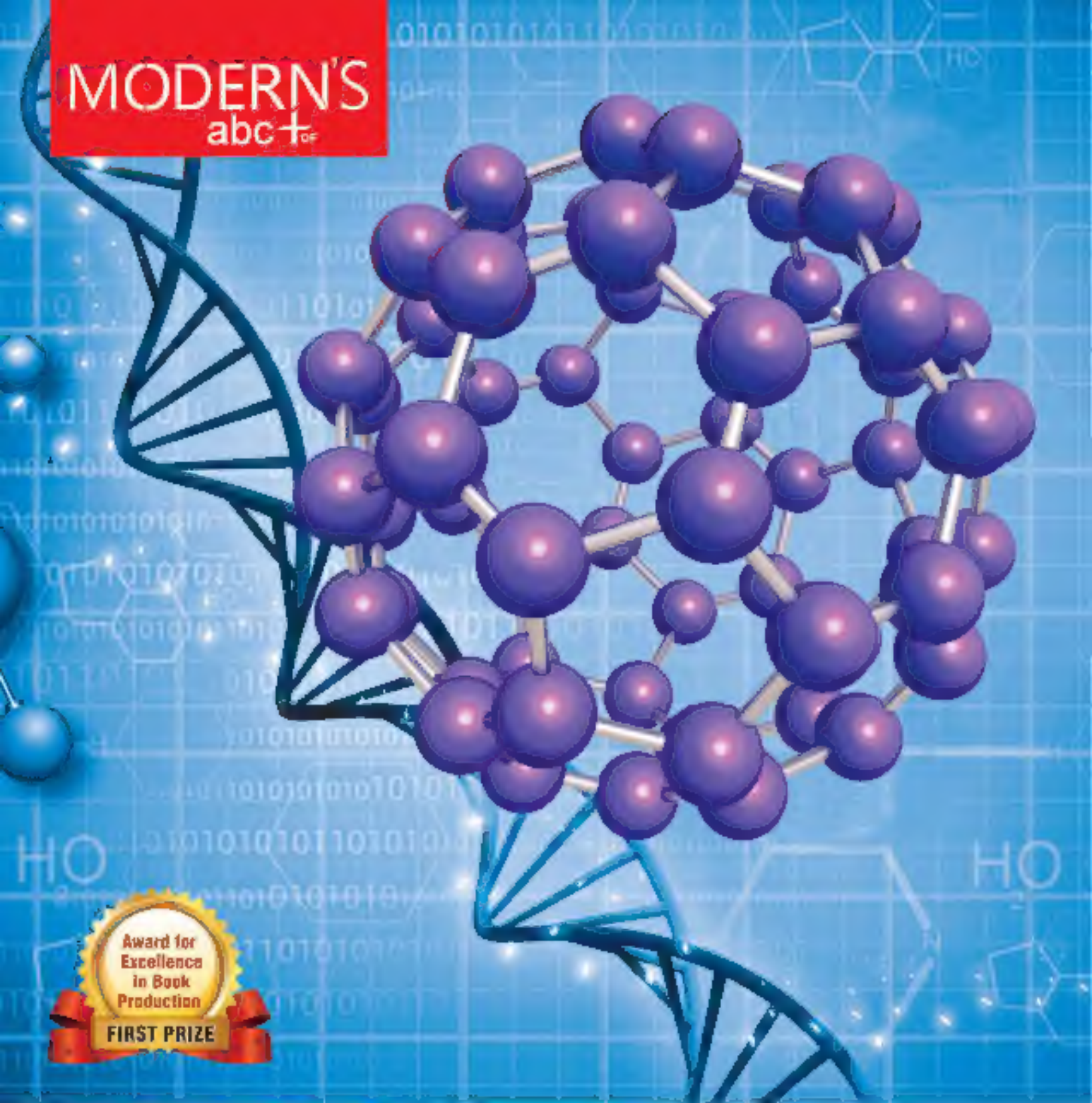


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CHEMISTRY

CLASS-XII

PART-I & II

STRICTLY ACCORDING TO THE NEW SYLLABUS
INDIA'S FIRST SMART BOOK



Dr. S.P. Jauhar

According to new syllabus prescribed by Central Board of Secondary Education (CBSE), New Delhi and State Boards of Uttarakhand, Karnataka (IInd Year PUC), Chhattisgarh, Jharkhand, Punjab, Haryana, Himachal, Kerala, Mizoram, Meghalaya, Nagaland, Assam, Manipur and other States following CBSE & ISC curriculum.

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INDIA'S FIRST SMART BOOK

Strictly
in accordance
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Guidelines and Syllabus
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For Class XII

PART-II

By

Dr. S.P. JAUHAR

Formerly Professor of Chemistry
Department of Chemistry
Panjab University, Chandigarh



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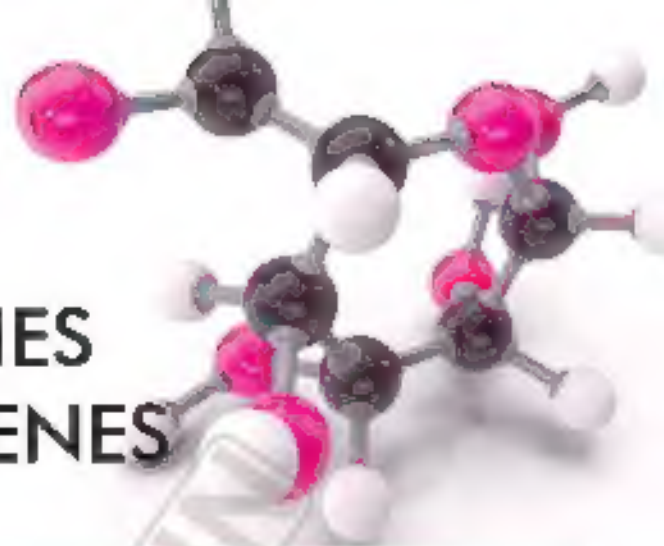
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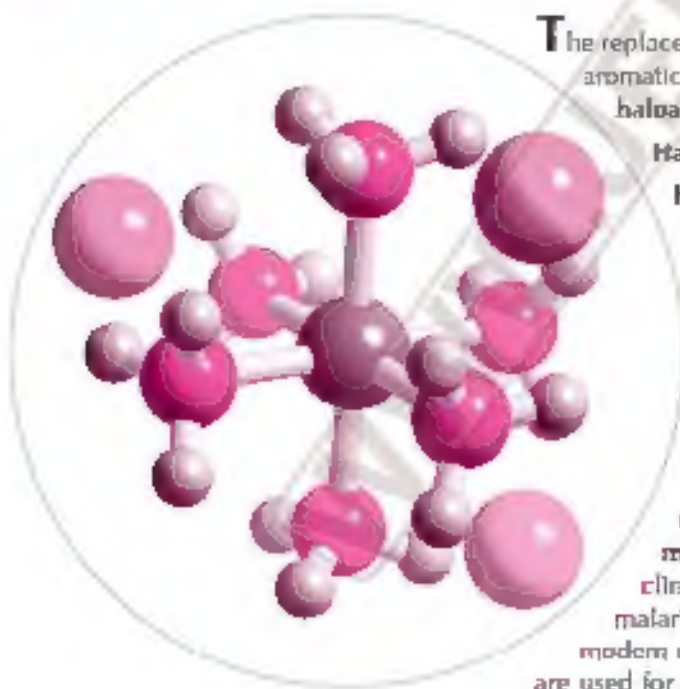


HALOALKANES AND HALOARENES



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The replacement of one or more hydrogen atoms of a hydrocarbon, aliphatic or aromatic, by an equal number of halogen atoms results in the formation of **haloalkanes** (or **alkyl halides**) and **haloarenes** (or **aryl halides**) respectively.

Haloalkane : RX where R is *alkyl group*

Haloarene : ArX where Ar is *arene*. X is halogen atom (F , Cl , Br , I)

Thus, haloalkanes and haloarenes are **halogen derivatives of aliphatic and aromatic hydrocarbons**.

Haloalkanes contain halogen atom(s) attached to the sp^3 hybridised carbon atom(s) of an alkyl group whereas haloarenes contain halogen atom(s) attached to sp^2 hybridised carbon atom(s) of aryl group.

These classes of compounds find wide applications in industry as well as in our day-to-day life. Some naturally occurring halogen containing organic compounds are important in **health care** and **medicine**. Some synthetic organic halogen compounds are also clinically useful. For example, *chloroquine* is used for the treatment of malaria and *halothane* ($CF_3CHClBr$) is used in surgery as an anaesthetic. In modern electronics industry, halogenated solvents such as trichloroethylene are used for cleaning semiconductors, chips and other components.

Above all, these organic halogen compounds are used as important starting materials for the synthesis of a wide range of other substances.

CLASSIFICATION OF HALOGEN DERIVATIVES OF HYDROCARBONS

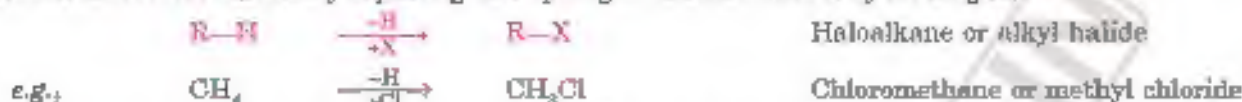
The halogen derivatives of hydrocarbons are broadly classified into two simple types :

1. Aliphatic halogen compounds
2. Aromatic halogen compounds

1. Aliphatic halogen compounds

These are the compounds which are obtained by the replacement of one or more hydrogen atoms of an aliphatic hydrocarbon by an equal number of halogen atoms. These can be further classified on the basis of the nature of aliphatic hydrocarbon, whether alkanes, alkenes or alkynes as haloalkanes, haloalkenes or haloalkynes, respectively.

(i) **Haloalkanes** : The halogen derivatives of alkanes are called **haloalkanes**. These are also called **alkyl halides**. These are formed by replacing one hydrogen atom in alkane by a halogen.



The general formula of haloalkanes or alkyl halides is $\text{C}_n\text{H}_{2n+1}\text{X}$ or commonly written as RX where R is an alkyl group and X is a halogen atom (F, Cl, Br or I and $n = 1, 2, 3 \dots$).

Some common examples are :

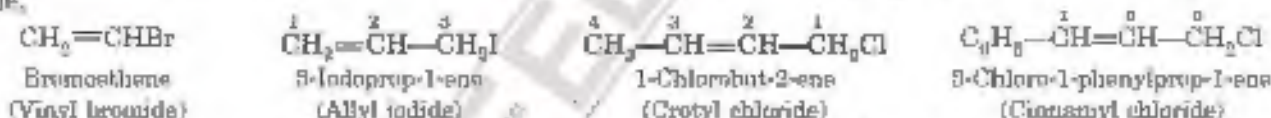
CH_3Cl Chloromethane (Methyl chloride)	$\text{CH}_3\text{CH}_2\text{Br}$ Bromoethane (Ethyl bromide)	$\text{CH}_3\text{CH}_2\text{CH}_2\text{Cl}$ Chloropropane (n-Propyl chloride)	$\text{CH}_3\text{CH}_2\text{I}$ Iodoethane (Ethyl iodide)
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NOTE

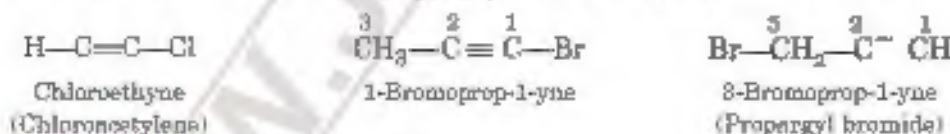
Whenever, two names are given under the formula, the name outside the brackets refers to IUPAC name and the name given in the brackets refers to the common name.

The compounds are also known in which more than one hydrogen atoms of the alkane molecule have been replaced by halogen atoms. These compounds are called polyhalogen derivatives of alkanes or **polyhaloalkanes**.

(ii) **Haloalkenes or alkenyl halides**. The halogen derivatives of alkenes are called **haloalkenes** or **alkenyl halides**. The monohalogen derivatives of alkenes have the general formula $\text{C}_n\text{H}_{2n-1}\text{X}$ where $\text{X} = \text{F}, \text{Cl}, \text{Br}$ or I . For example,



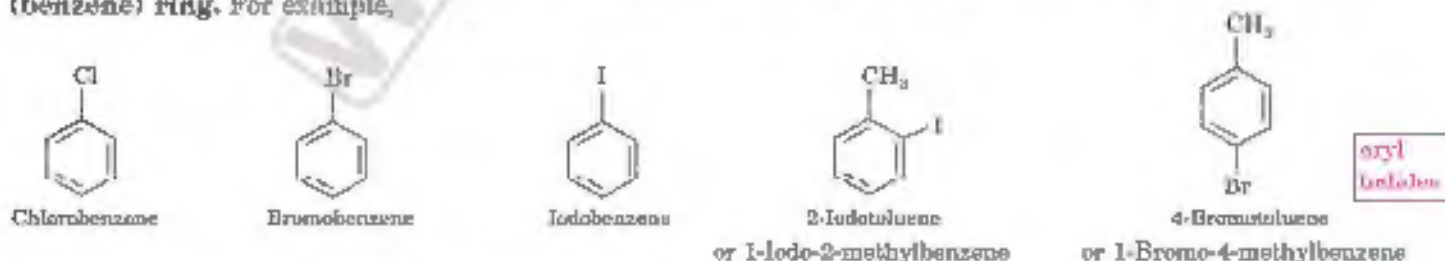
(iii) **Haloalkynes or alkynyl halides**. These are the halogen derivatives of alkynes. The monohalogen derivatives of alkynes have the general formula $\text{C}_n\text{H}_{2n-2}\text{X}$, where $\text{X} = \text{F}, \text{Cl}, \text{Br}$ or I . For example,



2. Aromatic halogen compounds

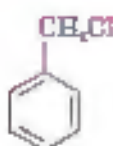
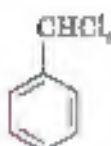
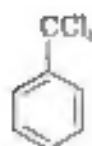
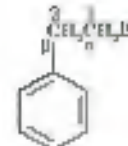
These are the compounds which are obtained by the replacement of one or more hydrogen atoms of aromatic hydrocarbons by an equal number of halogen atoms. These are of two types :

(i) **Nuclear halogen derivatives**. These are the halogen derivatives of aromatic hydrocarbons which are derived by replacing hydrogen atom attached to the benzene ring by a halogen atom. These are also called **haloarenes** or **aryl halides**. Therefore, in haloarenes, the halogen atom (F, Cl, Br or I) is directly bonded to the aromatic (benzene) ring. For example,



The aryl halides are commonly written as Ar-X , where Ar (short name for aryl) represents a phenyl group.

(ii) **Side chain halogen derivatives**. These are the derivatives of aromatic hydrocarbons in which one or more atoms of the alkyl side chain of a benzene are replaced by the halogen atoms. These compounds are not regarded as aryl halides because halogen is not directly attached to the benzene ring. These are called **side chain substituted aryl halides** or **aralkyl halides**. For example,

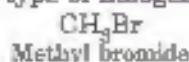
1-Chloro-1-phenylethane
(Benzyl chloride)1, 1-Dichloro-1-phenylethane
(Benzal dichloride)1, 1, 1-Trichloro-1-phenylethane
(Benzo trichloride)1-Bromo-2-phenylethane
(β -phenylethyl bromide)

aralkyl
halides

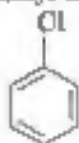
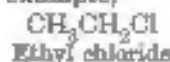
These haloalkanes or haloarenes may be simply classified on the basis of the type of halogen atom present, the number of halogen atoms and the nature of carbon atom to which the halogen is attached.

A. Type of halogen atom

The halogen derivatives of hydrocarbons may be classified as fluoro, chloro, bromo and iodo compounds depending upon the type of halogen present. For example,



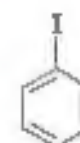
Fluorobenzene



Chlorobenzene



Bromobenzene

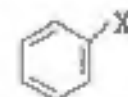
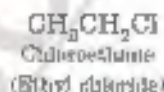
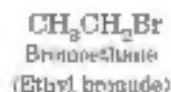


Iodobenzene

B. Number of halogen atoms

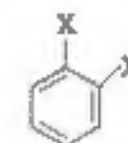
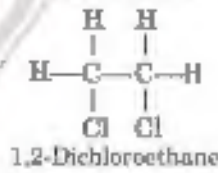
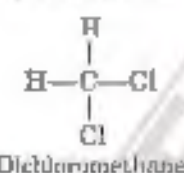
The halogen derivatives of hydrocarbons may be classified as mono, di, tri ... halo compounds depending upon whether they contain one, two, three... halogen atoms in their molecules. For example,

Monohalo compounds



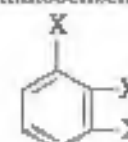
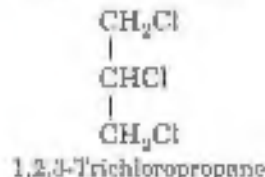
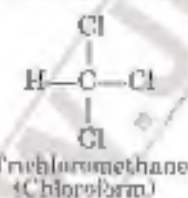
Monohalobenzene

Dihalo compounds



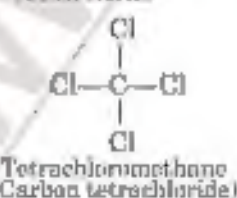
Dihalobenzene

Trihalo compounds



Trihalobenzene

Tetrahalo compounds



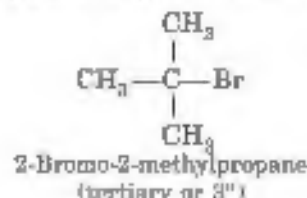
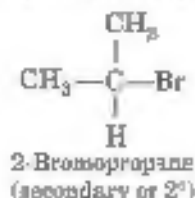
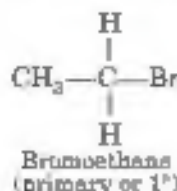
C. Nature of carbon atom

Haloalkanes are classified as *primary* (1°), *secondary* (2°) or *tertiary* (3°) depending upon the nature of carbon atom to which the halogen is attached.

(i) **Primary haloalkanes** are those which have *one or none alkyl group* on the carbon bonded to the halogen atom.

(ii) **Secondary haloalkanes** are those which have *two alkyl groups* on the carbon bonded to the halogen atom.

(iii) **Tertiary haloalkanes** are those which have *three alkyl groups* on the carbon bonded to the halogen atom.



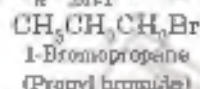
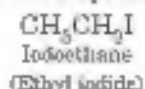
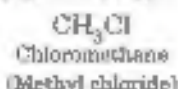
Classification on the basis of type of hybridization of carbon bonded to the halogen atom

The monohalo compounds may further be classified according to the type of hybridization of the carbon atom bonded to the halogen atom.

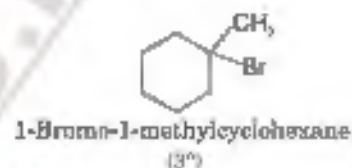
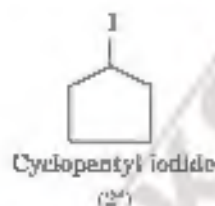
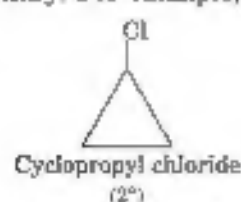
1. Compounds containing sp^3 hybridised carbon [$C(sp^3) - X$]

These compounds contain sp^3 hybridised carbon atom bonded to a halogen atom ($X = F, Cl, Br, I$). These are of the following types :

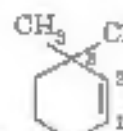
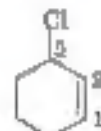
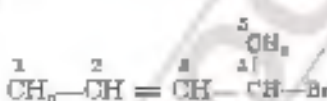
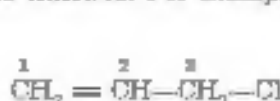
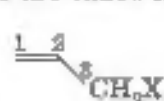
(a) **Halalkanes or alkyl halides (RX)**. In these halides, the halogen atom (X) is bonded to an alkyl group (R). These form homologous series of compounds represented by $C_nH_{2n+1}X$. For example,



If R is alicyclic in $R-X$, the halide is called cyclo alkyl halide or halocyclo alkane, which may be secondary or tertiary. For example,



(b) **Allylic halides**. In these halides, the halogen is bonded to an sp^3 hybridized carbon atom next to a carbon-carbon double bond. The carbon atom next to carbon-carbon double bond is called allylic carbon and therefore, these are called **allylic halides**. For example,



3-Haloprop-1-ene (1°)
(Allyl halide)

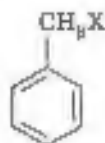
3-Chloroprop-1-ene (1°)

4-Bromopent-2-ene
(3°)

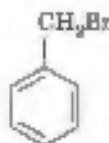
3-Chlorocyclohex-1-ene
(2°)

3-Chloro-3-methylcyclohex-1-ene

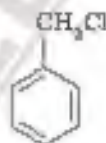
(c) **Benzylic halides**. In these halides the halogen atom is bonded to an sp^3 hybridised carbon atom next to an aromatic ring i.e., to a benzylic carbon. For example,



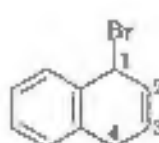
Halophenylmethane
(Benzyl halide) (1°)



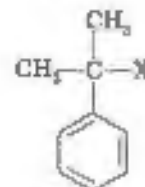
Bromophenylmethane
(1°)



Chlorophenyl methane
(1°)



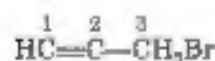
1-Bromo-1,2,3,4-tetrahydronaphthalene (2°)



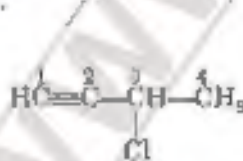
2-Halo-2-phenylpropane (3°)

It may be noted that allylic and benzylic halides may be primary (1°), secondary (2°) or tertiary (3°).

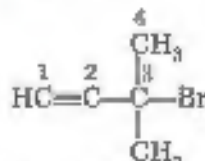
(d) **Propargyl halides**. In these halides, the halogen atom is bonded to a sp^3 hybridised carbon atom next to a carbon-carbon triple bond.



3-Bromoprop-1-yne
(Propargyl bromide)
(1°)



3-Chlorobut-1-yne
(2°)



3-Bromo-3-methylbut-1-yne
(3°)

2. Compounds containing sp^2 hybridised carbon [$C(sp^2)-X$]

These halogen derivatives of hydrocarbons contain sp^2 hybridised carbon. In these compounds, halogen is directly bonded to one of the carbon atoms of a double bond ($-\text{C}=\text{C}-\text{X}$). These include :

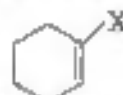
(a) **Vinyl halides**. In these halides the halogen atom is bonded to an sp^2 hybridised carbon of one of the carbon atoms of a double bond i.e. vinylic carbon. For example,



Haloethene
(Vinyl halide)



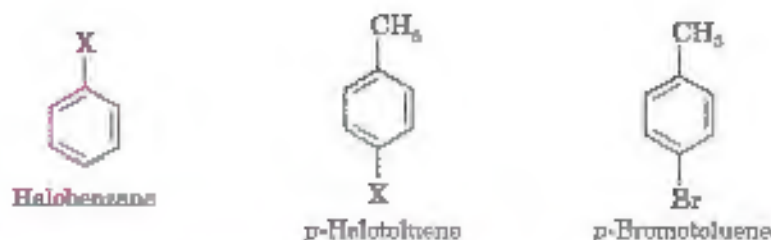
Chloroethene
(Vinyl chloride)



1-Halocyclohex-1-ene

(b) **Aryl halides**. In these halides, the halogen atom is bonded to a sp^2 hybridised carbon of an aromatic ring.

For example,



These aromatic halogen compounds are also called **haloarenes**.

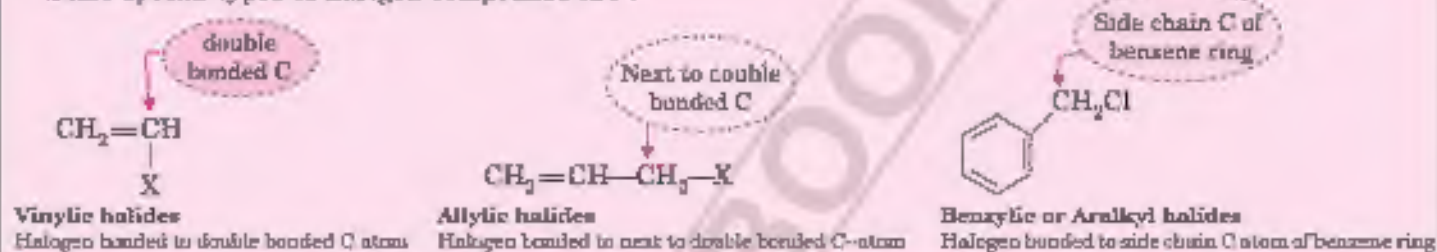
ii. Compounds containing *sp* hybridised carbon ($C(sp) - X$)

These halogen derivatives of hydrocarbons contain *sp* hybridised carbon. In these halogen derivatives, halogen is directly bonded to one of the carbon atoms of a triple bond ($-C \equiv C-X$). For example,



REMEMBER

Some special types of halogen compounds are :



Let us discuss the chemistry of **alkyl halides** and **aryl halides**.

NOMENCLATURE OF HALOALKANES AND HALOARENES

Naming haloalkanes (or alkyl halides)

Monohalogen derivatives

Common Names : In the **common** or **trivial system** the monohalogen derivatives of alkanes are called **alkyl halides**. These are named by naming the **alkyl group** attached to **halogen** and adding the name of the **halide**. For example,

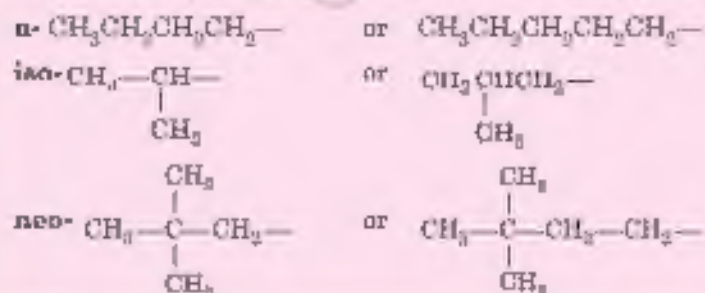


The name of the alkyl and halide is always written as two separate words. The prefixes *n*-, *iso*-, *sec*-, *tert*-, etc. used for the alkyl group are also written.

► It may be noted that *sec*- or *tert*- compounds are written with a dash between *sec*- or *tert*- and the name of the alkyl group. For example, *tert*-butyl, etc. However, the *iso*- or *neo*- compounds are written as one word. For example, isobutane, neopentane, etc.

REMEMBER

The prefixes **n**-, **iso**-, **neo**- are used for the following alkyl groups :



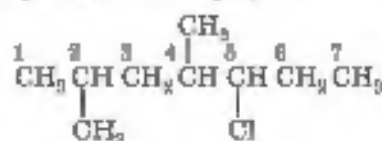
The prefix **n**- is used for alkyl group having continuous chain of C-atoms with no branching.

The prefix **iso**- is used for those alkyl groups in which one methyl group is attached to the next to end C-atom.

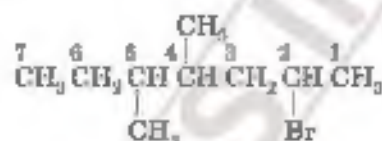
The prefix **neo**- is used for those alkyl groups which have two methyl groups attached to the next to end C-atom.

IUPAC names : In the IUPAC system, the monohalogen derivatives of alkanes are named as **haloalkanes**. The names are written by prefixing the word **halo** to the name of the alkane corresponding to longest continuous carbon chain holding the halogen atom. In case of branched chain alkanes, the following rules are followed :

- Select the longest continuous chain containing the carbon attached to the halogen group and name it as the **parent chain**. If a double or triple bond is present, the parent chain must contain it.
 - Number the carbon atoms of the parent chain, beginning from the end nearer to the first substituent, **regardless of whether it is alkyl or halo group**.
 - If two or more substituents are present on the parent chain, these are named in the alphabetical order alongwith their appropriate positions.
- It may be noted that di, tri, tetra etc. are not considered while comparing the substituents for alphabetizing purpose. For example,

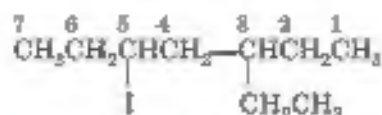
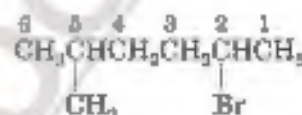


5-Chloro-2, 4-dimethylheptane



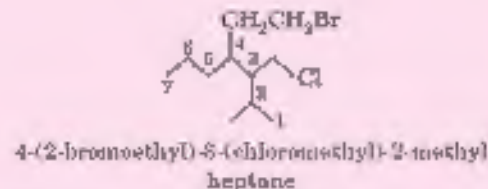
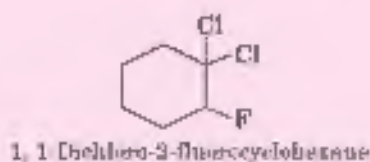
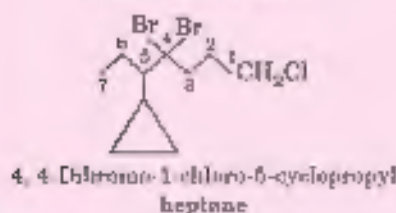
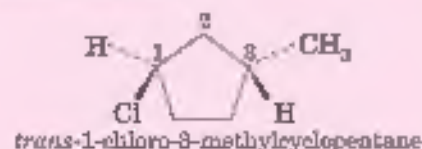
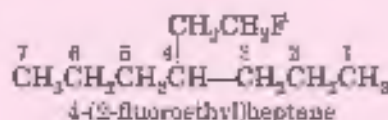
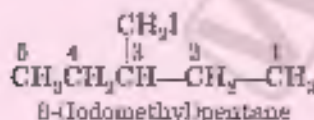
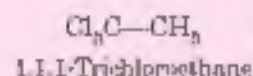
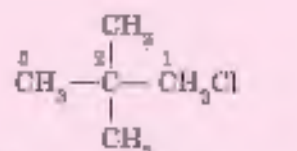
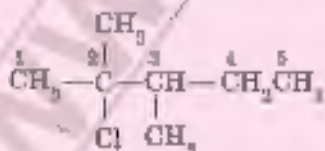
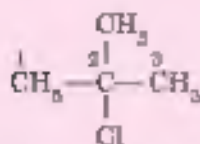
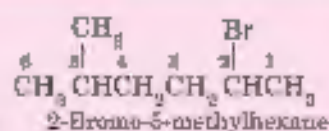
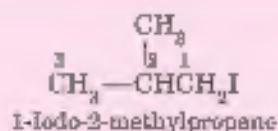
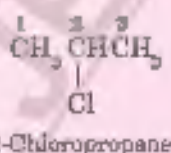
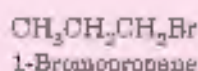
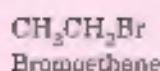
2-Bromo-4, 5-dimethylheptane

- If two different substituents are present at **equivalent positions** from the two ends of the chain, then numbering the chain is done in such a way that the substituent which comes first in the alphabetical order (written first in the name) gets lower number. For example,

3-Ethyl-5-iodoheptane
(Not 5-Ethyl-3-iodoheptane)2-Bromo-5-methylhexane
(Not 5-Bromo-2-methylhexane)

[For more rules see Appendix A]

To illustrate the rules, some examples are given below:



The common and IUPAC names of a few alkyl halides are given below

Alkyl halide	Common name	IUPAC name
CH_3Cl	Methyl chloride	Chloromethane
$\text{CH}_3\text{CH}_2\text{Br}$	Ethyl bromide	Bromoethane
$\text{CH}_3\text{CH}_2\text{CH}_2\text{F}$	<i>n</i> -Propyl fluoride	1-Fluoropropane
$\text{CH}_3\text{CH}(\text{CH}_3)\text{I}$	Isopropyl iodide	2-Iodopropane
$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{Cl}$	<i>n</i> -Butyl chloride	1-Chlorobutane
$\text{CH}_3\text{CH}(\text{CH}_3)\text{CH}_2\text{Cl}$	<i>sec</i> -Butyl chloride	2-Chlorobutane
$\text{CH}_3\text{CH}(\text{CH}_3)\text{CH}_2\text{Cl}$	Isobutyl chloride	1-Chloro-2-methylpropane
$\text{CH}_3\text{C}(\text{CH}_3)_2\text{CH}_2\text{Cl}$	<i>tert</i> -Butyl chloride	2-Chloro-2-methylpropane
$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{Cl}$	<i>n</i> -Pentyl chloride or <i>n</i> -Amyl chloride	1-Chloropentane
$\text{CH}_3\text{CH}(\text{CH}_3)\text{CH}_2\text{CH}_2\text{Cl}$	Isopentyl chloride or Isamyl chloride	1-Chloro-3-methylbutane
$\text{CH}_3\text{C}(\text{CH}_3)_2\text{CH}_2\text{CH}_2\text{Cl}$	<i>tert</i> -Pentyl chloride or <i>tert</i> -Amyl chloride	2-Chloro-2-methylbutane
$\text{CH}_3\text{C}(\text{CH}_3)_3\text{CH}_2\text{Cl}$	Neopentyl chloride or Neoamyl chloride	1-Chloro-2,2-dimethylpropane

NOTE

Amyl is commonly used for C_5H_{11} group. The prefixes *iso*, *neo*, *cyclo* are written as non-hyphenated prefixes while *is*, *sec* or *tert* are written as hyphenated prefixes.

Dihalo and polyhalo derivatives

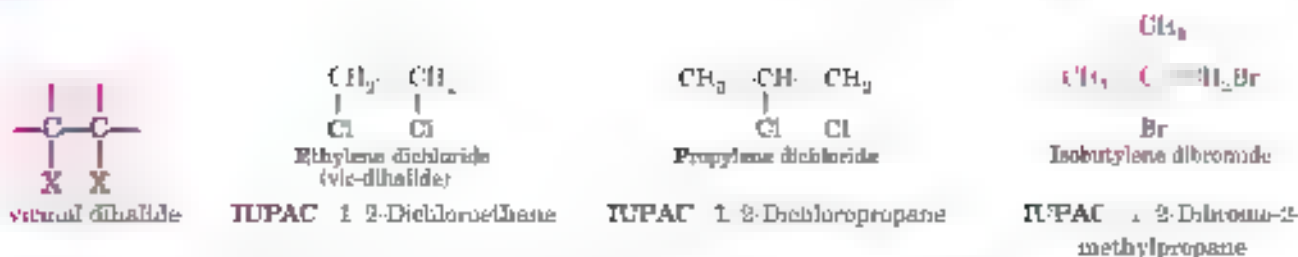
The dihalo derivatives have special common names depending upon whether the halogen atoms are present on the same or different carbon atoms. These are commonly named according to IUPAC system.

- a) When both the halogen atoms are attached to the same C-atom, these are called **gem-dihalides**. These are also called **alkylidene dihalides** or simply **alkylidene halides**. For example

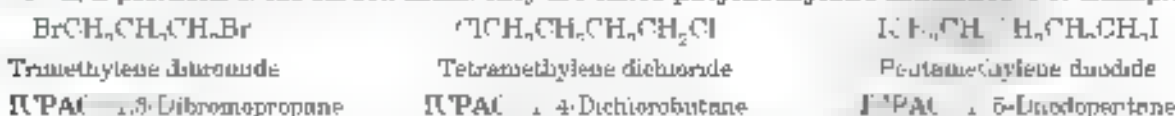


gem dihalide IUPAC 1,1-Dichloroethane IUPAC 2,2-Dichloropropane IUPAC 1,1-Dichloropropane

- b) When the two halogen atoms are on adjacent C-atoms, they are called **vicinal dihalides** or simply **vic-dihalides**. These are named as the dihalides of alkene from which they may be prepared by the addition of halogen atoms i.e., **alkylene dihalide** or simply **alkylene halide**. For example,

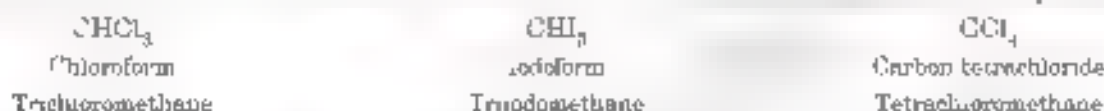


iii. **Polymethylene dihalides.** When the same two halogen atoms are present on the terminal carbon atoms i.e. α, ω positions of the carbon chain, they are called **polymethylene dihalides**. For example,

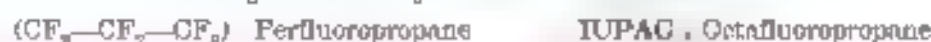


Polyhalogen derivatives are named according to IUPAC system.

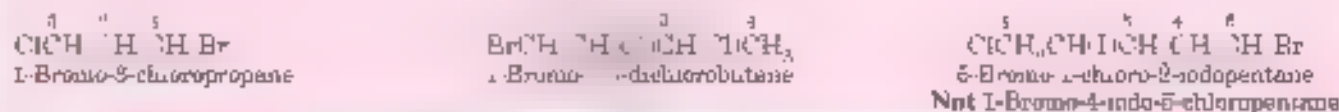
Trihalomethanes and tetrahalomethanes are named as haloforms and carbon tetrahalides respectively



Fully halogenated hydrocarbons are also called **perhalohydrocarbons** per means that all the hydrogens of the hydrocarbons are replaced by halogen atoms. It may be noted that polyhaloalkanes and other complex halogen compounds are named according to IUPAC system.



It may be noted that the name of di- and polyhaloalkanes containing different halogen atoms are written by prefixing the name of each halogen atom in any order along with its locant to the name of the parent alkane. The lowest locant being given so that halogen atom which comes first in alphabetical order *provided it does not violate the lowest locant sum rule*. For example,

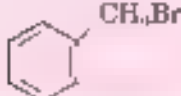


HELP

The compound $\text{ClCH}_2\text{CH}_2\text{ICH}_2\text{CH}_2\text{CH}_2\text{Br}$ cannot be named 1-Bromo-4-iodo-6-chloropentane because it violates lowest set of locants rule.

Some of these are given in Table 1.

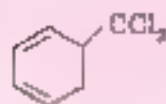
Table 1 Common names and IUPAC names of polyhaloalkanes and complex halogen compounds.

Structure	Common name	IUPAC name
CH_2Cl_2	Methylene chloride	Dichloromethane
$\text{CH}_2=\text{CHCl}$	Vinyl chloride	Chloroethene
$\text{CH}_3-\text{CHCH}_2\text{Br}$	Allyl bromide	1-Bromopropane
$\text{CH}_2=\text{CH}_2$	Ethylene chloride	1,2-Dichloroethane
CH_2CHCl_2	Ethylene chloride	1,1-Dichloroethane
CHCl_3	Chloroform	Trichloromethane
CHI_3	Iodoform	Triiodomethane
CHBr_3	Bromoform	Tri bromomethane
	Benzyl bromide	1-Bromo-1-phenylmethane



Benzal dichloride

1,1-Dichloro-1-phenylmethane



Benzotrichloride

1,1,1-Trichloro-1-phenylethane



Perfluoropropene

Octafluoropropene

Naming haloarenes or aryl halides)

Haloarenes or aryl halides are named by adding the prefix *halo-* (fluoro-, chloro-, bromo-, iodo-) before the name of the aromatic hydrocarbon. In case of disubstituted compounds, the relative positions of the substituents 1, 2, 1, 3 and 1, 4 are indicated by the prefixes *ortho* (*o*-), *meta* (*m*-) and *para* (*p*-) respectively. For example

Cl



Chlorobenzene

Br



Bromobenzene

I



Iodobenzene

Cl

1,2-Dichlorobenzene
o-DichlorobenzeneCH₃1-Chloro-2-methylbenzene
2-Chlorotoluene
o-Chlorotoluene

Br



1-Bromo-3-chlorobenzene

CH₃1-Chloro-3-methylbenzene
m-ChlorotolueneCH₃1-Chloro-4-methylbenzene
4-Chlorotoluene
p-Chlorotoluene

Cl

1,4-Dichlorobenzene
p-Dichlorobenzene

Br

1,3,5-Tribromobenzene
(*sym*-Tribromobenzene)**REMEMBER****Special names**

Vinyl



Allyl



Phenyl



Benzyl



Benzal

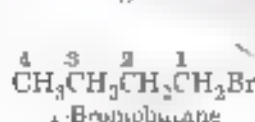


Benzoyl

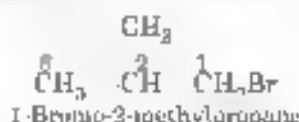
ISOMERISM IN HALOALKANES AND HALOARENES

Haloalkanes show two types of isomerism:

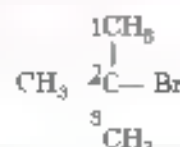
1. **Chain isomerism.** The haloalkanes containing four or more carbon atoms exhibit chain isomerism in which the isomers differ in the chain of carbon atoms. For example, C_4H_9Br has three chain isomers as



1-Bromobutane



1-Bromo-2-methylpropane



2-Bromo-2-methylpropane

2. **Position isomerism.** The haloalkanes containing three or more carbon atoms exhibit position isomerism in which the isomers differ in the position of halogen atom. For example, C_3H_7I has two position isomers

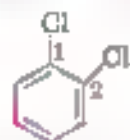


1-Iodopropane

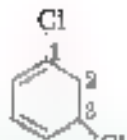


2-Iodopropane

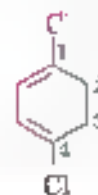
Haloarenes also show position isomerism as



1,2-Dichlorobenzene
(o-Dichlorobenzene)



1,3-Dichlorobenzene
(m-Dichlorobenzene)

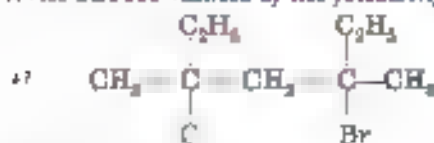


1,4-Dichlorobenzene
p-Dichlorobenzene

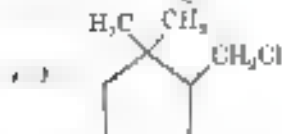
SOLVED EXAMPLES

Example 1

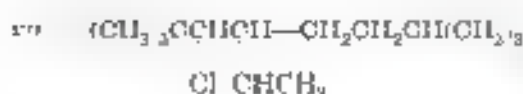
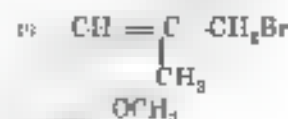
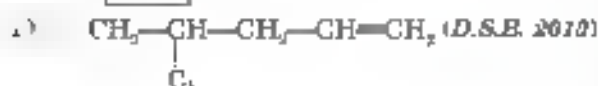
Write IUPAC names of the following compounds



(D.S.B. 2011)



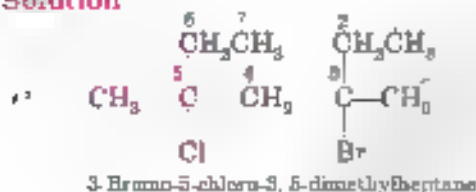
(D.S.B. 2012)



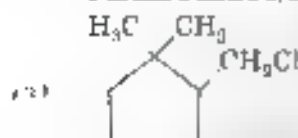
(A.I.S.B. 2018)



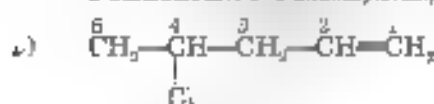
Solution



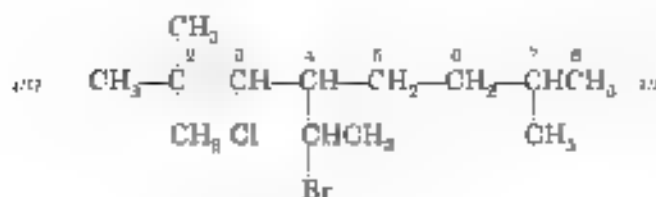
3-Bromo-5-chloro-3,5-dimethylheptane



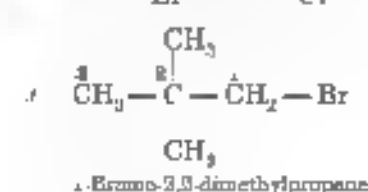
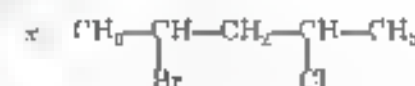
1-Chloro-2,2-dimethylcyclopentane



4-Chloropent-1-ene



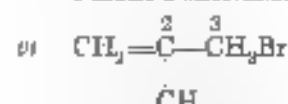
4-(1-Bromoethyl)-3-chloro-2,2,7-trimethylheptane



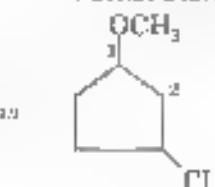
1-Bromo-2,3-dimethylpropane



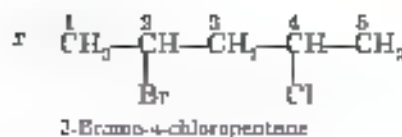
1-Bromo-2-iodocyclobutene



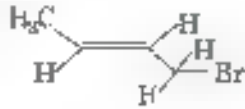
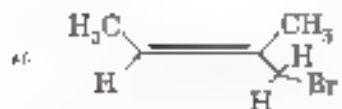
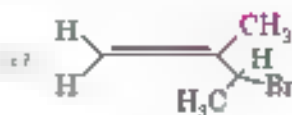
3-Bromo-2-methylpropene



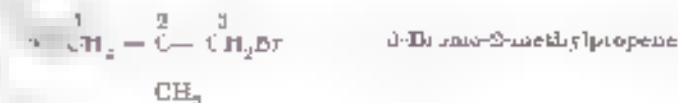
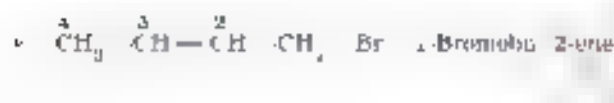
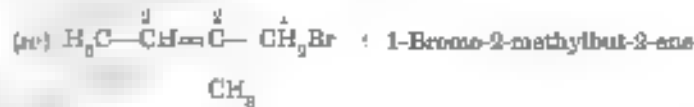
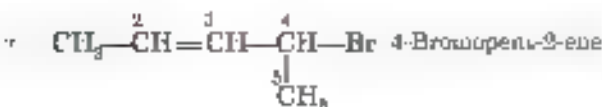
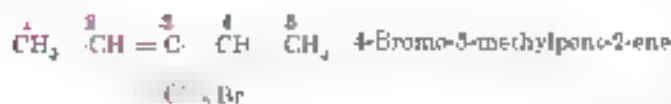
1-Chloro-3-methoxycyclopentane


Example 2.

Write IUPAC names of the following compounds



[N.C.E.R.T.]

Solution

Example 3.

Write the structures of the following compounds

(i) 2-Chloro-3-methylpentane

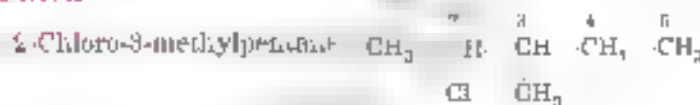
(ii) 1-Chloro-4-ethylcyclohexane

(iii) 4-tert Butyl 3-iodoheptane

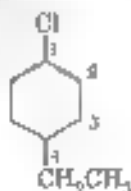
[N.C.E.R.T.]

(iv) 1,4-Dibromobut-2-ene

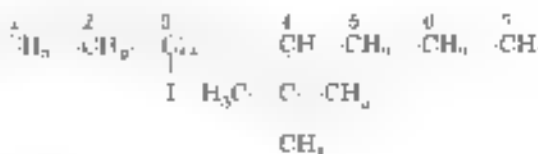
(v) 1-Bromo-4-sec-butyl 2-methylbenzene

Solution


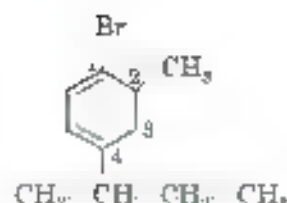
(ii) 1-Chloro-4-ethylcyclohexane



(iii) 4-tert Butyl 3-iodoheptane



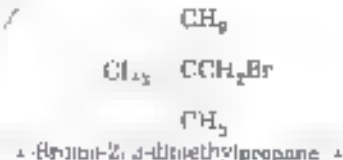
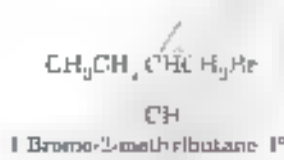
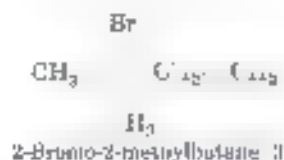
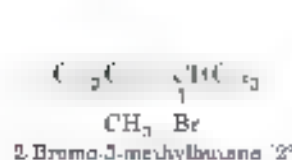
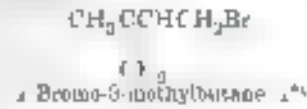
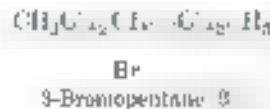
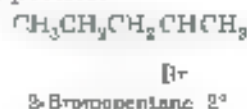
(v), 1-Bromo-4-sec-butyl-2-methylbenzene



Example 4.

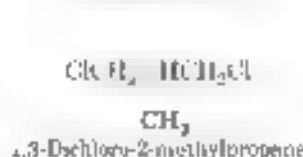
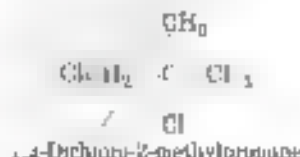
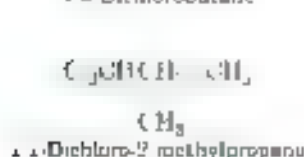
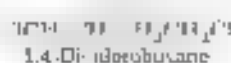
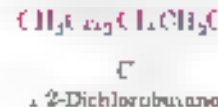
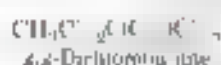
Draw the structures of all the eight structural isomers that have the molecular formula $C_5H_{11}Br$. Name each isomer according to the IUPAC system and classify them as primary, secondary or tertiary. (N.C.E.R.T.)

Solution Eight isomers are possible.



Example 5.

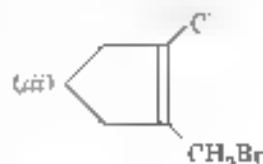
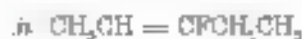
Write structural formulae and give IUPAC names of isomers of $C_4H_8Cl_2$.



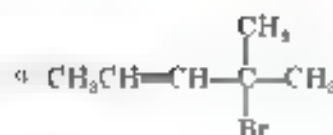
Practice Problems

- Give the structural formula and IUPAC names of *sec*-isobutyl iodide & *tert*-amyl bromide & *sec*-butyl bromide.
- Write the structures of the following compounds and identify them as 1° 2° or 3° halides.
 - 1-Bromo-2-methylpropane
 - 2-chloro-2-methylpropane
 - 2-Bromo-3-methylbutane
 - 3-Bromopentane
 - 2-Bromo-2-methylbutane
 - Neopentyl chloride
- Write the structures of the following dichloroalkanes and identify them as gem or vicinal. (any)
 - 2,3-Dichlorobutane
 - 2,2-Dichlorobutane
 - 1,4-Dichlorobutane
 - 1,2-Dichlorobutane
 - 1,3-Dichloro-3-methylpropane
- Write all the possible isomers of compound C_4H_9Br and give their IUPAC names.
- Classify the following as aryl, vinyl, allyl or aryl halides.

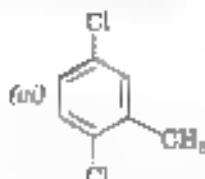
Hr. S.B. 2019



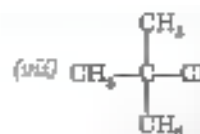
6. Write IUPAC names of the following compounds



(H.S.B. 2013)

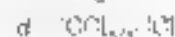


(A.I.S.B. 2012)



(H.S.B. 2014)

7. Write the IUPAC names of the following compounds



Answers to Practice Problems



CH_3
1-Iodo-2-methylpropane



Br
2-Bromo-2-methylbutane

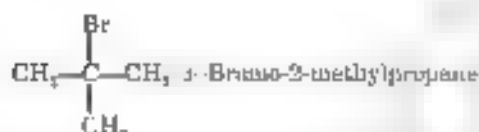


Br
2-Bromobutane

2. (a) 1° (b) 3° (c) 2° (d) 2° (e) 3° (f) 1°

3. (a) vicinal (b) gem (c) vicinal

4. $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{Br}$ 1-Bromobutane $\text{CH}_3\text{CH}_2\underset{\text{Br}}{\text{CH}}\text{CH}_3$ 2-Bromobutane $\text{CH}_3\underset{\text{CH}_3}{\text{CH}}\text{CH}_2\text{CH}_2\text{Br}$ 1-Bromo-2-methylpropane



5. (i) allyl (ii) vinyl (iii) vinyl chloride and allyl bromide

(iv) alkyl (v) allyl (vi) aryl

6. (i) 1-Bromo-1-chloro-1,2,2-trifluoroethane

(ii) 1-Bromo-4-chlorobut-2-yne

(iii) 4-Bromo-4-methylpent-2-ene

(iv) 1-Chloro-3-methylbut-2-ene

(v) 4-(1-Bromoethyl)-1-chloro-2,2,7-trimethyloctane

(vi) 1,4-Dichloro-2-methylbenzene

(vii) 2-Chloro-2-methylpropane

7. (a) 2-Bromo-2-chlorobutane

(b) 1-Bromo-1-chloro-1,2,2-trifluoroethane

(c) 1-Bromo-4-chlorobut-3-yne

(d) 3-Trichloromethyl-1,1,2,3,3,3-hexachloropropane

(e) 2,2-bis(4-chlorophenyl)-3-bromobutane

(f) 1-chloro-4-(4-iodophenyl)-3,3-dimethylbut-1-ene

(g) 2,5,5-Trifluoroheptane

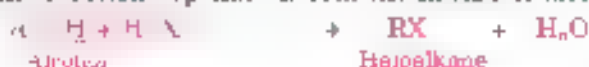
METHODS OF PREPARATION OF HALOALKANES OR ALKYL HALIDES

Haloalkanes are generally prepared in the laboratory by the following methods

1. From Alcohols

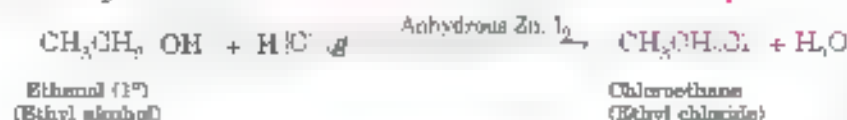
This is the most widely used method for the preparation of haloalkanes in the laboratory. The hydroxy group $-\text{OH}$ of an alcohol is replaced by the halogen atom (X) by reaction with concentrated halogen acids, phosphorus halides or thionyl chloride. This can be done by the following methods

(a) By the action of halogen acids. Alcohols can be converted into haloalkanes by treatment with halogen acids (HX). However, the rate of the reaction depends on both the nature of alcohol and the halogen acid.



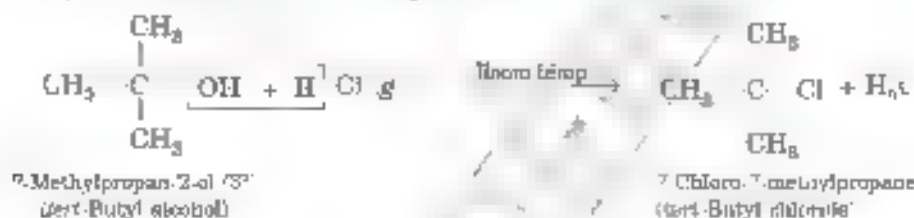
For example,

• Primary and secondary alcohols form **chloroalkanes** when hydrochloric acid gas is passed through alcohol in the presence of anhydrous zinc chloride. This is known as **Lucas's process**.

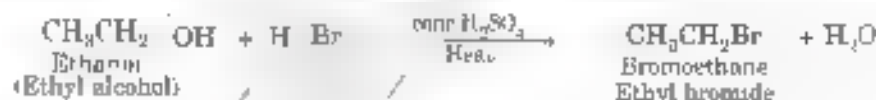


The purpose of anhydrous ZnCl_2 is to help in the cleavage of the $\text{C}-\text{O}$ bond. ZnCl_2 is a Lewis acid and therefore, it readily coordinates with the oxygen atom of the alcohol. As a result, the $\text{C}-\text{O}$ bond weakens and finally breaks to form carbocation. The carbocation, then readily reacts with chloride ion to form chloroalkanes.

Tertiary alcohols, are **very reactive** and therefore, they react readily simply by shaking with conc. HCl even in the absence of zinc chloride at room temperature.



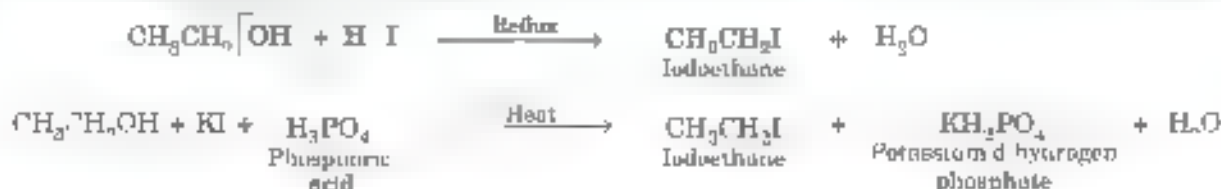
Bromoalkanes are obtained in a similar manner by refluxing a suitable alcohol with hydronbromic acid 48% in the presence of a conc. H_2SO_4 which acts as a catalyst.



HBr being unstable can also be generated *in situ* during the reaction by the action of conc. H_2SO_4 on KBr or NaBr .



• **Iodoalkanes** are obtained by heating alcohols with constant boiling hydriodic acid 57%. Like HBr , HI can also be generated *in situ* during the reaction by the action of 85% phosphoric acid in potassium iodide.



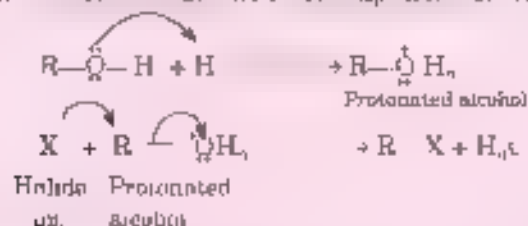
HELP

Refluxing is a process of heating a liquid in a flask provided with a condenser. The vapours of the liquid which rise up get condensed back into the flask.

It may be noted that unlike alkyl halides, secondary and tertiary bromides and iodides cannot be prepared from the respective alcohols. This is because secondary and tertiary alcohols on heating with conc. H_2SO_4 undergo dehydration to form alkenes.

Hydrogen fluoride is the least reactive of the hydrogen halides and the preparation of fluorides is not practical by this method.

The reaction is an example of nucleophilic substitution reaction in which nucleophile (halide ion) attacks the protonated alcohol with the expulsion of water, a good leaving group.



The order of reactivity of halogen acids with alcohols is



Since the nucleophilicity, i.e., the tendency to donate an electron pair to carbon atom of the halide ions increases in the order $\text{I}^- > \text{Br}^- > \text{Cl}^-$, the order of reactivity of halogen acids increases in the same order, i.e., $\text{HI} > \text{HBr} > \text{HCl}$. This order is also in accordance with the bond dissociation enthalpies of $\text{H}-\text{X}$ bonds. The bond dissociation enthalpy of HI is less than that of HBr which is less than that of HCl .

Reactivity of alcohols is :



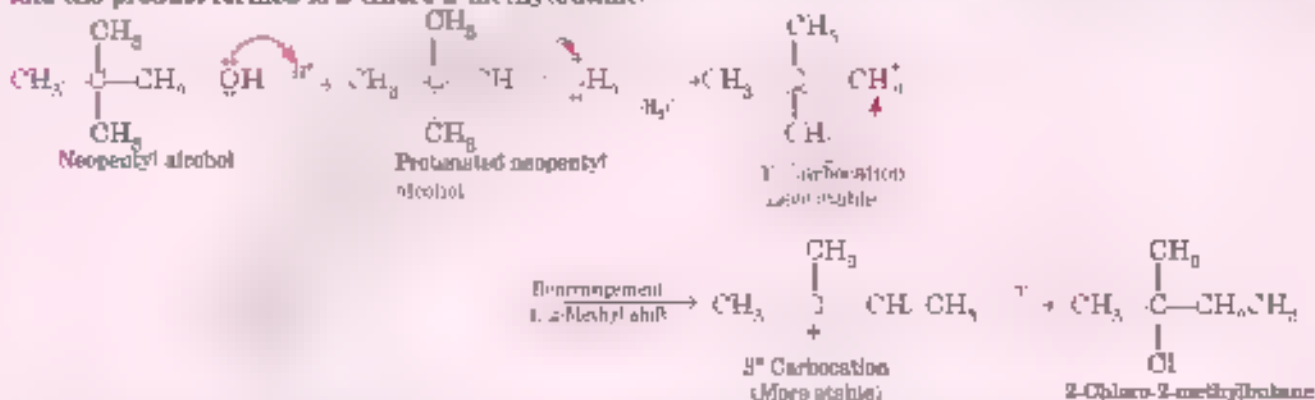
This is in accordance with the stability of carbocation formed in the transition state. The stability of carbocation decreases in the order $3^\circ > 2^\circ > 1^\circ$ and hence the order of reactivity of alcohols also decreases in the same order, i.e., $3^\circ > 2^\circ > 1^\circ$ alcohol.

The mechanism of this reaction is discussed in next unit.

Now Curious...

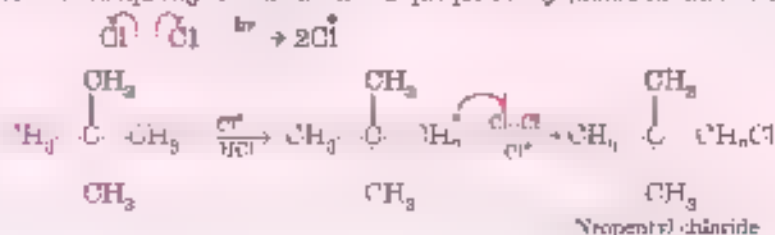


- Neopentyl chloride cannot be prepared by the action of HCl on neopentyl alcohol. It can be best prepared by photochemical chlorination of neopentane.
- Neopentyl chloride cannot be prepared by the action of HCl on neopentyl alcohol. This is because, the reaction occurs through the formation of carbocation. The neopentyl carbocation (1°) formed rearranges to 3° carbocation and the product formed is 2-chloro-2-methylbutane.



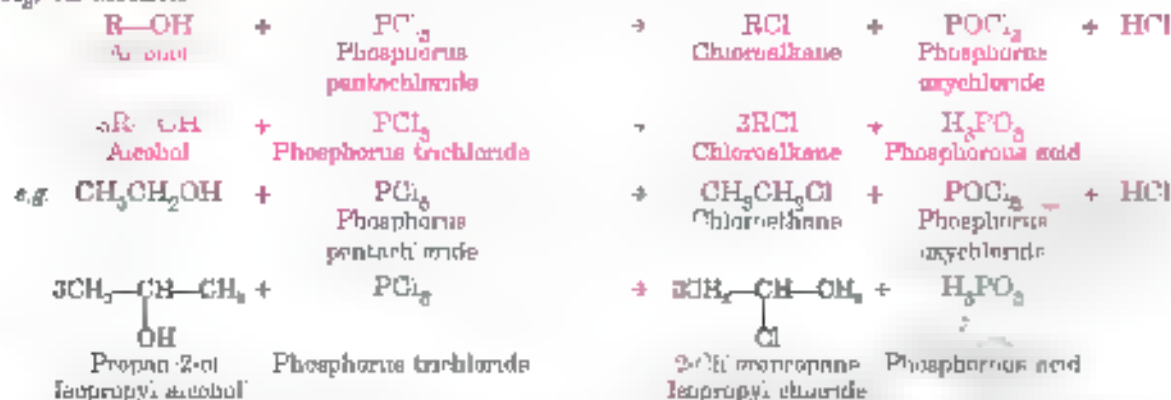
However, free radicals normally do not undergo rearrangement.

Therefore, neopentyl chloride can be prepared by photochemical free radical chlorination of neopentane.



(b) By the action of phosphorus halides. Haloalkanes can be prepared by the action of phosphorus halides on the alcohols.

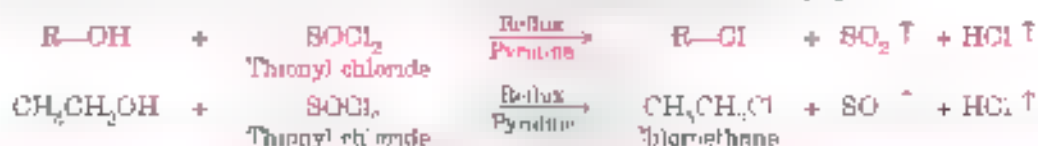
Chloroalkanes can be prepared by the action of phosphorus pentachloride PCl_5 or phosphorus trichloride (PCl_3) on alcohols.



Bromoalkanes and iodoalkanes are prepared by the action of phosphorus tribromide (PBr_3) and phosphorus triiodide (PI_3) respectively on alcohols. Since PBr_3 and PI_3 are not very stable compounds, these are generally prepared *in situ* by the action of red phosphorus on Br_2 or I_2 as



(c) By the action of thionyl chloride. Chloroalkanes can be prepared from alcohols by refluxing alcohols with thionyl chloride in the presence of an organic base, e.g. as pyridine ($\text{C}_5\text{H}_5\text{N}$).



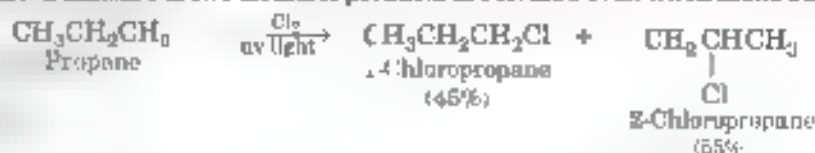
This method is preferred than other methods because both the products of the reaction SO_2 and HCl are gases and can easily escape leaving behind pure alkyl halide. Therefore the pure compounds can be prepared easily.

2. From Hydrocarbons

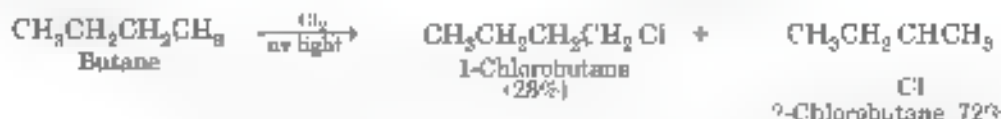
The haloalkanes can be prepared from alkanes, alkenes and alkynes by the replacement of hydrogen atom by halogen atom.

A. From alkanes

Alkyl halogens (Cl_2 and Br_2) react with alkanes in the presence of ultraviolet light to form haloalkanes. This reaction is free radical substitution reaction. It gives a mixture of mono, di or polyhaloalkanes from alkanes which are difficult to separate into pure components. Moreover, the yield of any one compound is low because of the formation of other compounds. For example, in case of propane, a mixture of two isomeric products are formed even when mono substitution is carried out.



Similarly

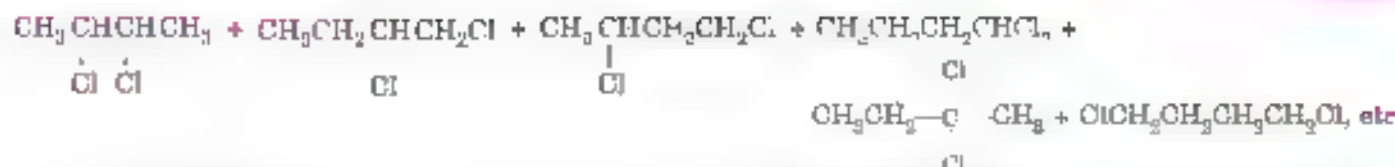


The relative amounts of these isomeric haloalkanes depend upon the nature of the halogen (Cl_2 or Br_2) and the number and type of hydrogen (1° , 2° or 3°) being substituted. In general, the ease of substitution of various hydrogens follows the sequence



However, their relative rates vary with the nature of halogen. For example, with Cl_2 , the relative rates of substitution of 3° , 2° and 1° hydrogens at 298K is 5 : 3.8 : 1 whereas with Br_2 at 400 K these are 1000 : 82 : 1.

In addition to above monohalo compounds, isomeric dihalo and trihalo compounds are also possible.



Therefore, halogenation of alkanes is not a suitable method for laboratory preparation of haloalkanes. This is mainly because a mixture of different isomers are formed which are difficult to separate. However, free radical substitution is still useful in certain cases as discussed below.

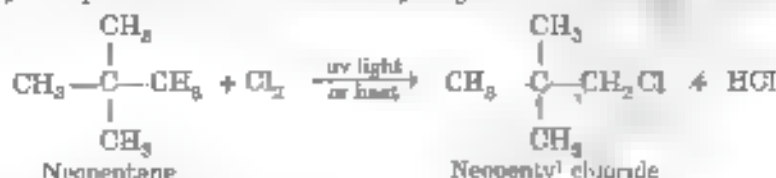
When the mixture of products can be easily separated by some suitable method. For example, chlorination of methane gives different products which have suitable differences in the boiling points. Therefore, these can be separated by fractional distillation.



Thus,



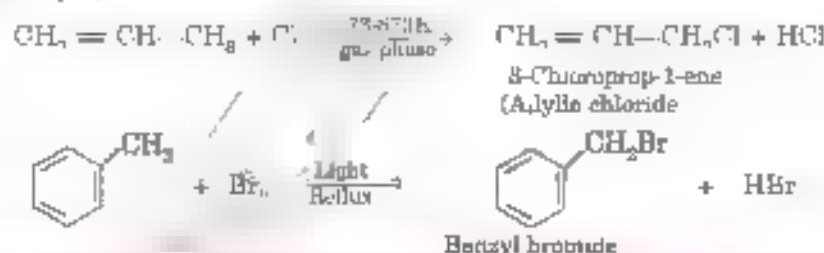
ii When the structure of alkane is such that the formation of isomeric product is not possible. For example, neopentane gives only one product because all the hydrogen atoms are equivalent.



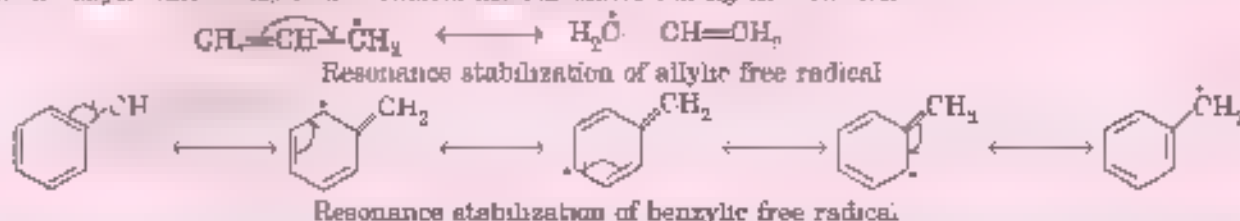
iii When there is a large difference in the reactivity of hydrogens attached to different types of carbon atoms, only one product is formed under suitable conditions. For example, the reactivity of different types of hydrogens in halo compounds are

Benzylic = allylic > alkyl > vinylic = aryllic

This is opposite to the homolytic bond dissociation enthalpies. The vinylic and aryllic hydrogens are so unreactive that they do not participate in free radical halogenation reactions. Thus allylic and benzylic halides can be easily prepared. For example,



The high reactivity of allylic and benzylic hydrogen atoms can also be explained in terms of stabilisation by resonance of the allylic and benzylic free radical intermediates during the reaction.



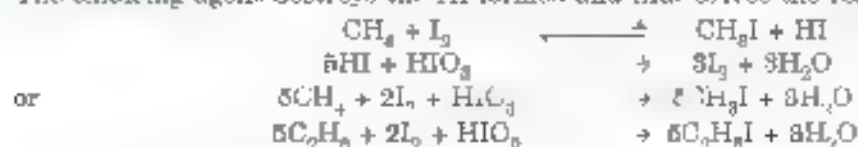
HELP

The 'half headed' curved arrows \curvearrowright represent movement of a single electron.

iv When pure products are not required especially when haloalkanes are used as solvents. The mixture of isomers is just suitable as a pure compound and is much cheaper. If needed, the product mixture can be separated into useful fractions by fractional distillation. By adjusting the proportion of the reactants, one of the products can be made to predominate which can be separated in good yield and purity. For example, methyl chloride can be obtained as a major product by using large excess of methane. The unreacted methane can be separated and reused. The chloro and bromo derivatives of methane are prepared industrially by this method.

b) The fluorination of alkanes with fluorine is highly exothermic and violent. This leads to pyrolysis and results into cleavage of carbon-carbon bonds. Alternatively alkyl fluorides are more conveniently prepared indirectly by halogen exchange method as discussed later.

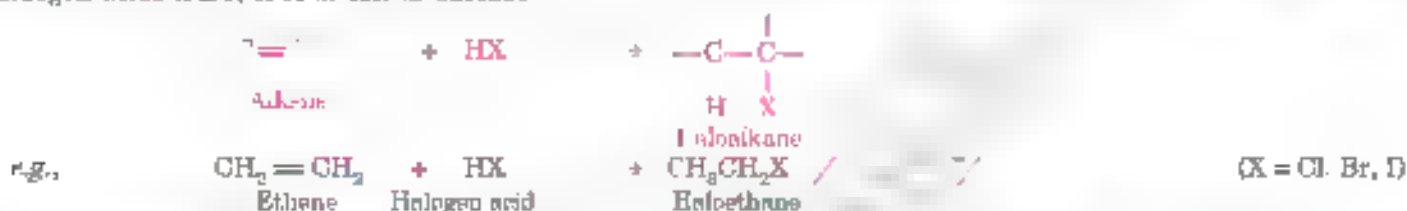
c) Iodination is reversible but it may be carried out in the presence of an oxidising agent such as H_2O_2 , HNO_3 , etc. The oxidising agent destroys the HI formed and thus drives the reaction towards the forward direction.



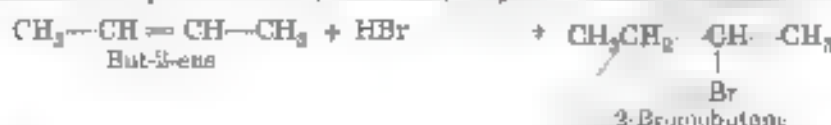
Iodination stops at monosubstituted stage.

B. From alkenes

a) Addition of hydrogen halides or halogen acids. Haloalkanes can be prepared by the electrophilic addition of halogen acids (HBr, HCl or HI) to alkenes.



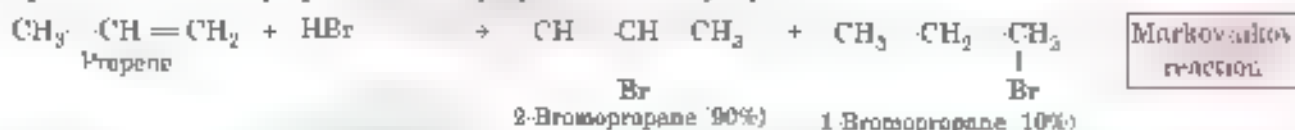
It may be noted that in case of addition to symmetrical alkenes ($\text{HC}=\text{CH}$), the carbon atoms joined by the double bond are equivalent and, therefore, only one addition product is formed. For example,



During the addition of halogen acids to unsymmetrical alkenes, **Markovnikov's rule** follows. According to this rule

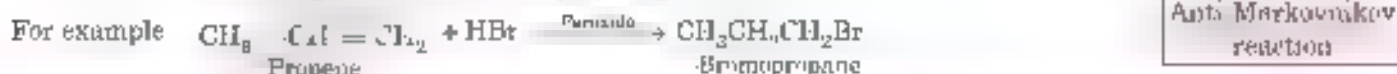
during the addition across unsymmetrical double bond, the negative part of the attacking reagent attaches itself to the carbon atom carrying lesser number of hydrogen atoms while the positive part goes to the carbon atom with more number of hydrogen atoms.

For example, in the case of propene 2-bromopropane is the major product.

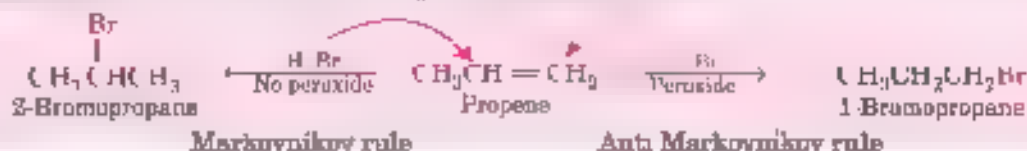


However, it has been observed that when HBr is added to an unsymmetrical double bond in the presence of organic peroxides such as benzoyl peroxide ($\text{C}_6\text{H}_5\text{---O---O---C}_6\text{H}_5$), the reaction takes place contrary to the Markovnikov's rule. This is known as **anti-Markovnikov's rule** or **peroxide effect**. It is also called **Kharasch effect**. According to anti-Markovnikov's rule

in the case of addition of HBr to unsymmetrical alkene, the negative part of the attacking reagent (Br) will join to the carbon atom carrying more hydrogen atoms while H-atom will go to the other carbon atom containing lesser number of hydrogen atoms.



Thus, different haloalkanes are obtained from unsymmetrical alkenes as



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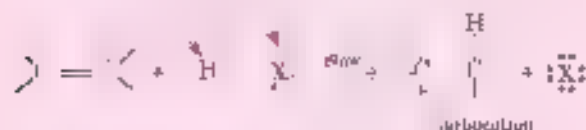
It may be noted that the anti-Markovnikov's rule or peroxide effect applies to the addition of HBr only and not to the addition of HI or HCl.

Markovnikov rule and Anti-Markovnikov Rule

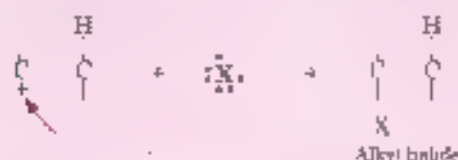
Mechanism of Markovnikov rule

The addition of HX to an alkene occurs by the following steps

Step 1 The alkene donates a pair of electrons to the proton of the hydrogen halide and forms a carbocation.

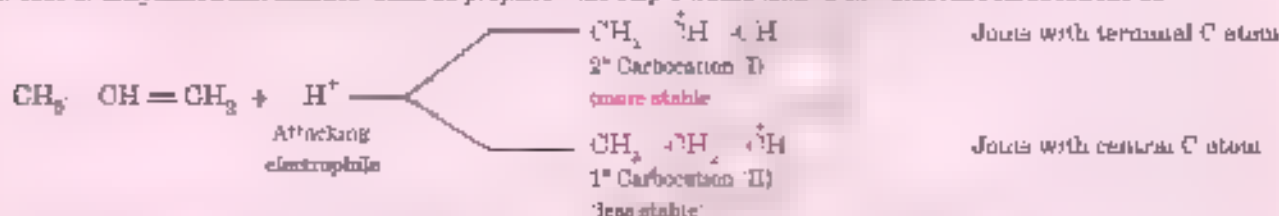


Step 2 The carbanion reacts with halide ion forming alkyl halide

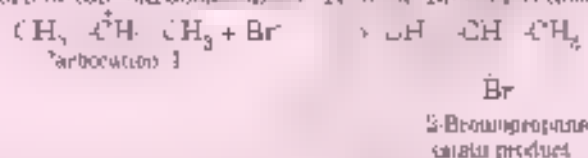


Theoretical Explanation of Markovnikov Rule

In case of unsymmetrical alkenes such as propene the step 1 would result in two different carbocations as



The carbocation that is formed with a large proportion is decided on the basis of a relative stability. Now we know that 2° carbocation is more stable than 1° carbocation, therefore, the attack of H^+ on an propene results in the formation of more stable carbocation. It then further reacts with Br^- to form the addition product.

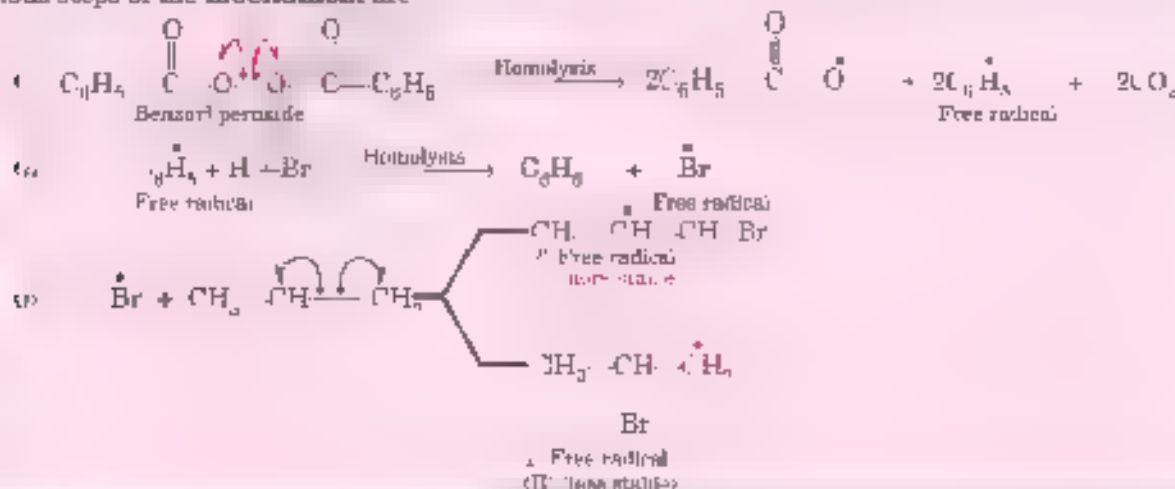


This product is in accordance with Markovnikov rule. Thus, Markovnikov rule may also be stated in the alternative form as

The electrophilic addition to an unsymmetrical alkene always occurs through the formation of a more stable carbocation intermediate.

Theoretical Explanation of Anti Markovnikov Rule or Peroxide Effect

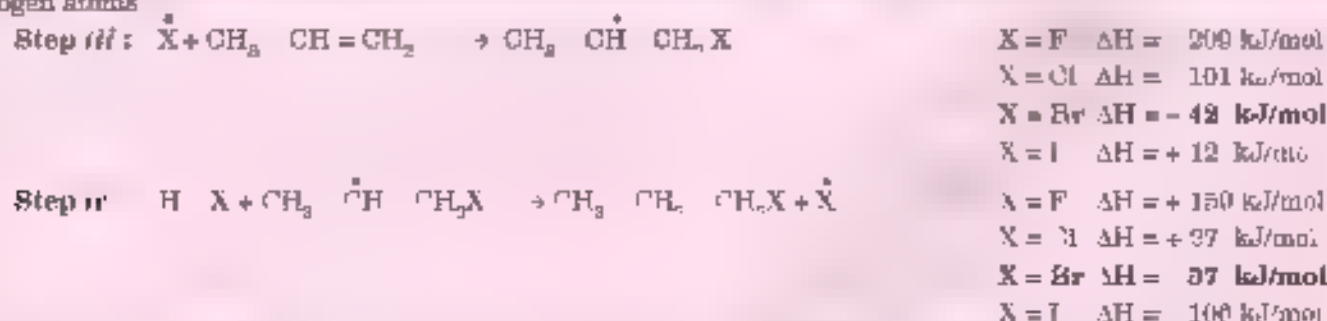
The addition of HBr to a ketene in the presence of peroxides occurs by **free radical mechanism**. In this mechanism the first two steps result in the generation of free radical Br^\cdot . Then, it adds to double bond in such a way to give more stable free radical. The α -free radical abstracts H^\cdot free radical from HBr to complete the addition. The various steps of the mechanism are



The step 2° gives two different free radicals. Since the 2° free radical is more stable than 1° free radical, it will be preferably formed giving the main product.

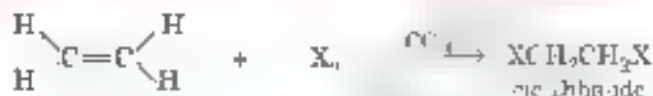


Exceptional behaviour of HBr. It is interesting to note that peroxide effect is applicable only to HBr and not to HF, H^+ or HI. This can be understood in the terms of energy changes in the propagation step using different halogen atoms.

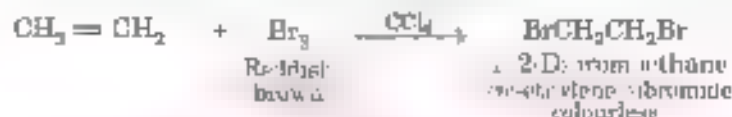


From the above data it is clear that only with HBr both the steps are **exothermic** and hence free radical mechanism is possible. With HF or HCl, the attack of these halos follows free radical mechanism because the second step involving the attack of carbon radical with HF or HCl is **endothermic** and is not favourable. In other words homolysis of HF or HCl does not take place. In case of HI the homolysis of HI is possible as evident from step 1, but the attack of I on propene does not take place. Step 2 is endothermic. So the free radical I will combine with similar free radical to form I_2 molecule. Thus, **peroxide effect is observed only in case of HBr**.

(7) Addition of halogens. When Br_2 or Cl_2 is added to alkenes, the addition occurs at the double bond forming a tetrahalide.

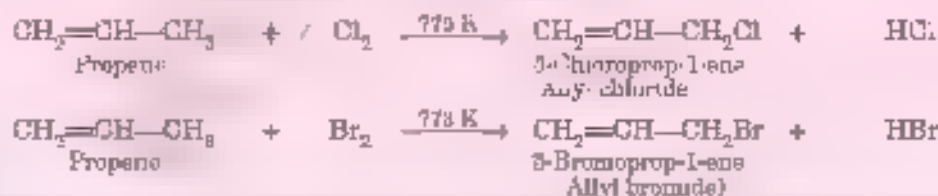


For example, when bromine in CCl_4 is added to ethene, the reddish brown colour of bromine gets discharged due to the formation of *cis*-dibromide, which is colourless. This is an **important test for the detection of double bond**.



Allylic substitution

When alkenes are heated with H_2 or Cl_2 at a high temperature of about 775 K, the hydrogen atom of any H carbon is substituted with halogen atom forming alkyl halides.



Such reactions in which halogenation occurs at the active position of an alkene are called **allylic halogenation reactions**.



R U Curious...

- ❑ **Halogens (Cl_2 or Br_2)** do not add to the double bond at high temperature but bring about substitution at allylic position.
- ▶ At high temperature the addition reaction of halogens to alkenes is reversible so that the addition product formed during the reaction undergoes dehalogenation. HX more rapidly than it is formed. However, at high temperature, the substitution reaction is irreversible and tends to produce allylic substitution products by a free radical mechanism.

3. By Halogen Exchange

This reaction is particularly useful for preparing **iodoalkanes**. The iodoalkanes are obtained by heating chloro or bromoalkanes with a concentrated solution of sodium iodide in acetone.



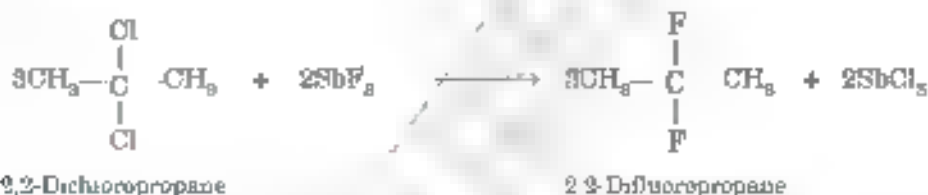
Sodium chloride and sodium bromide being less soluble in acetone get precipitated from the solution and can be removed by filtration. This also prevents the backward reaction to occur according to Le Chatelier's principle. The reaction gives the best results with primary halides.

This reaction is known as **Finkelstein reaction**.

Fluoroalkanes are **difficult** to prepare **directly**. These are prepared by treating alkyl chlorides or bromides with salts such as mercurous fluoride (Hg_2F_2), silver fluoride (AgF), cobalt fluoride (CoF_3) or antimony trifluoride (SbF_3). This reaction is known as **Swarts reaction**.



When the organic halides contain two or three halogen atoms on the same carbon atom, SbF_3 or CoF_3 are used. For example,



4. Preparation from Silver Salts of Acids

The silver salts of the carboxylic acids dissolved in CCl_4 are decomposed by bromine to form bromoalkanes. This reaction is called **Borodine Hunsdiecker reaction** or simply **Hunsdiecker reaction**. The reaction is believed to occur by free radical mechanism.



The yield of halide is **primary > secondary > tertiary** and bromine is generally used.

Chloroalkanes can also be obtained by this method by using Cl_2 instead of Br_2 , but the yield of chloroalkanes is very poor. Iodoalkanes cannot be obtained by this reaction because esters can be formed instead of iodoalkanes.

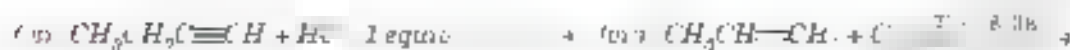


This is known as **Burnbaum Simonini reaction**.

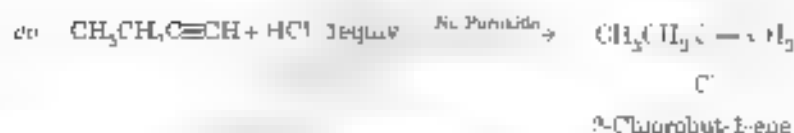
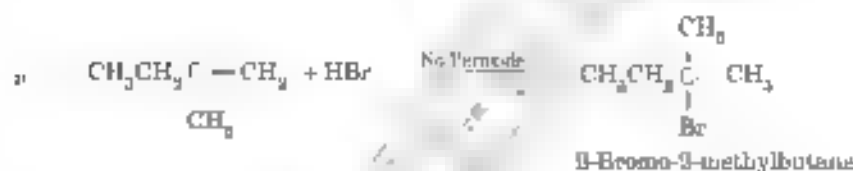
SOLVED EXAMPLES

□ Example 6.

Write the structure of the major product and IUPAC name in each of the following reactions



This reaction is called Finkelstein reaction.



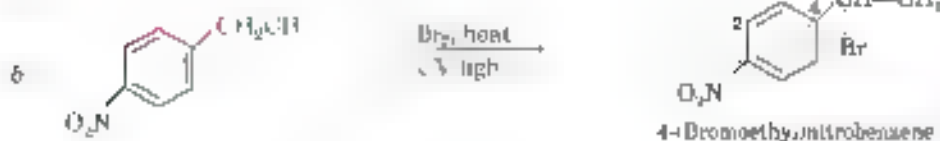
□ Example 7.

Draw the structures of major monohalo products in each of the following reactions





[NCERT]

**HELP**

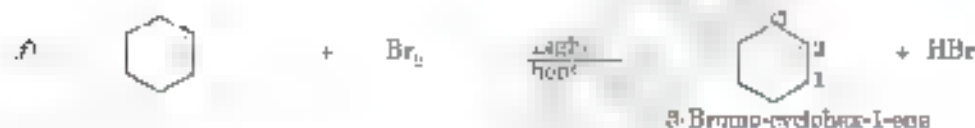
Since benzylic radicals are more stable, therefore benzylic H is abstracted

**HELP**

Only acetoic but not phenolic CH group is replaced by Cl on heating with HCl

**HELP**

I is a stronger nucleophile and hence displaces Br^- ion.

**HELP**

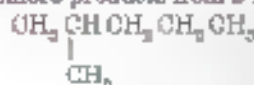
In the presence of high allylic bromination occurs to form 3-Bromo-cyclohex-1-ene

Example 8

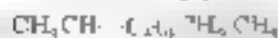
Draw and name the monochloro products you would expect to obtain from free radical chlorination of 2-methylpentane.

[NCERT]

Solution: Monochloro products from 2-methylpentane



1-Chloro-2-methylpentane



2-Chloro-2-methylpentane



1-Chloro-4-methylpentane



1-Chloro-3-methylpentane



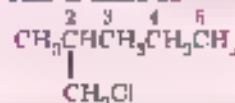
2-Chloro-4-methylpentane

Are You Curious...

Why cannot we get $\text{CH}_3\text{CH}(\text{CH}_3)\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{Cl}$?



► This is same as 2

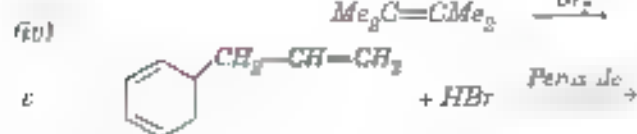
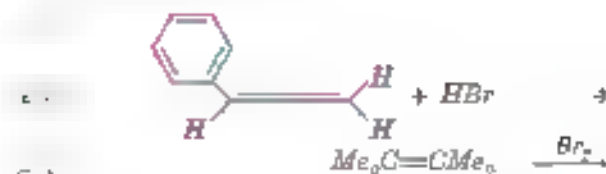


2-Chloro-2-methylpentane

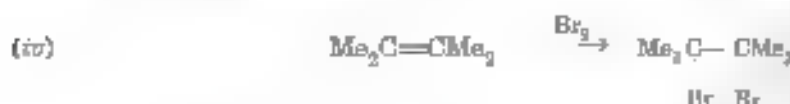
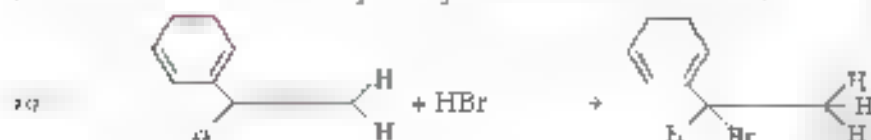
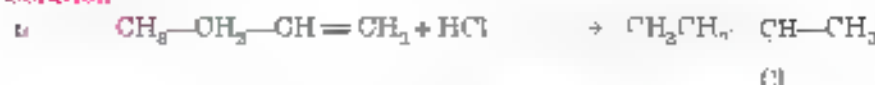
Example 9

Write the products of the following reactions





(A.I.S.B. 2018) [N.T.A.R.T.]

Solution

Practice Problems

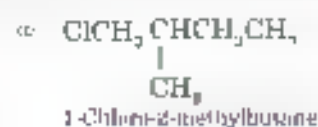
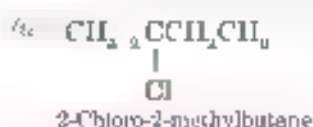
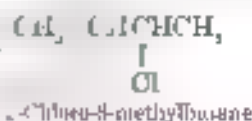
8. How will you prepare the following from an alcohol?

- (a) *sec*-Butyl bromide (b) *tert*-Butyl chloride (c) 2-Bromopropane
(d) 1-Bromopropane (e) Ethyl iodide (f) Fluoroethane

9. Identify all the possible monochloro structural isomers expected to be formed on free radical monochlorination of $\text{CH}_3\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}_3$.

[N.C.E.R.T.]

• Ans. There are four different types of hydrogen atoms. Replacement of these hydrogen atoms will give the following isomers



METHODS OF PREPARATION OF HALOARENES OR ARYL HALIDES

The common methods of preparation of haloarenes are given below

1. Direct halogenation or aromatic ring or electrophilic substitution of arenes

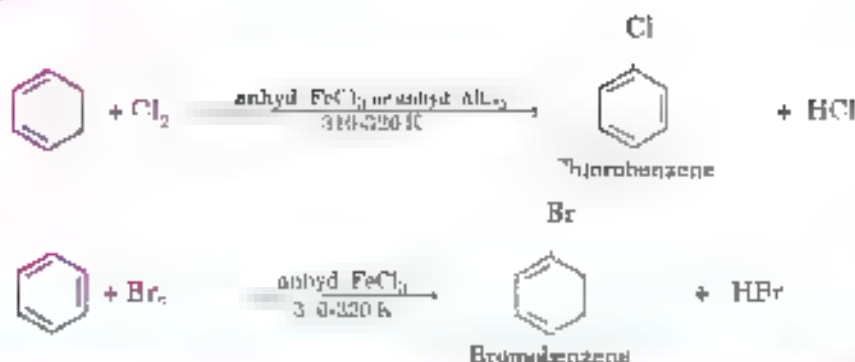
(a) **Nuclear halogenation.** Chloroarenes (aryl chlorides) and bromoarenes (aryl bromides) can be easily prepared by direct chlorination or bromination of benzene or other aromatic hydrocarbons. These reactions are carried out in dark at ordinary temperatures (310–320 K) in the presence of Lewis acid catalyst such as anhydrous ferric or aluminium halides (FeCl_3 , FeBr_3 , AlCl_3). These reactions are called **electrophilic substitution of arenes**.

The Lewis acid acts as a catalyst and its function is to carry the halogen to the aromatic hydrocarbon and is also called **halogen carrier**. In actual practice iron filings in the presence of chlorine or bromine are commonly used. The halogens react with iron filings to form corresponding Lewis acid as



[Aryl halide]





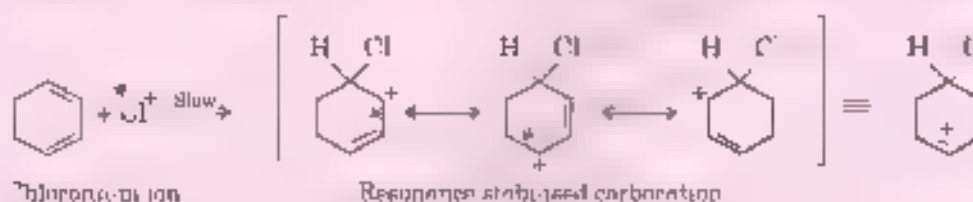
Functions of the Halogen Carrier and Mechanism of the Reaction

Halogenation of arenes is an **electrophilic substitution reaction**. The function of the halogen carrier is to generate **electrophile** which attacks the benzene ring to form the product. For example, the chlorination of benzene occurs as

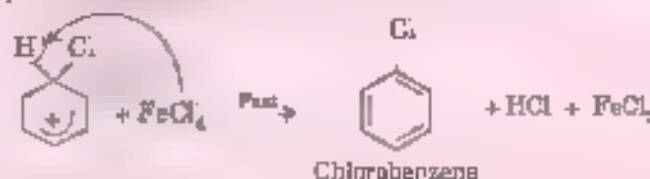
Step 1. Generation of electrophile: The electrophile is generated as



Step 2. Formation of carbocation (σ -complex) intermediate: The electrophile then attacks the benzene ring to form a carbocation (arenium ion or σ -complex) which gets resonance stabilised. **This is a slow and rate determining step**

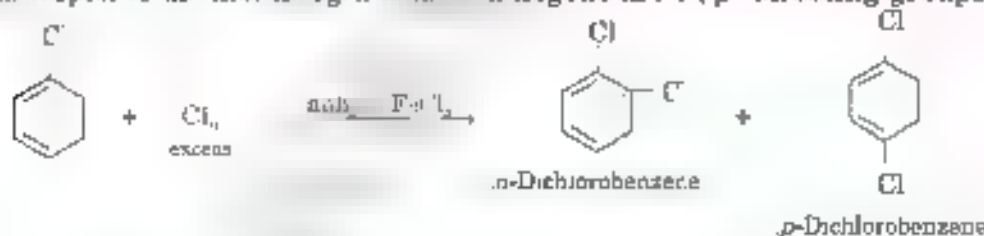


Step 3. Loss of proton from the carbocation intermediate: The resonance stabilised carbocation loses a proton (H^+) to FeCl_4 to give chlorobenzene. This is a fast step and therefore does not affect the rate of reaction.



This step is fast and hence does not affect the rate of the reaction.

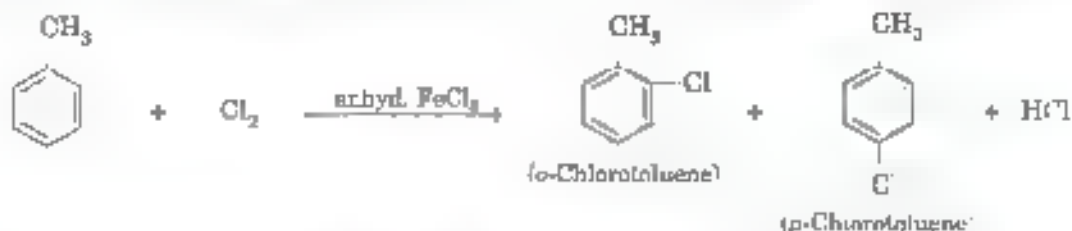
If excess of halogen is used, the second halogen also gets introduced in the ring mainly at *o*- and *p*-positions with respect to the first halogen because halogens are *o*-, *p*-directing groups.



REMEMBER

Halogen group is *ortho*, *para* directing group.

Chlorination of toluene gives a mixture of *o*- and *p*-chlorotoluene because CH_3 group is *ortho* and *para*-directing.

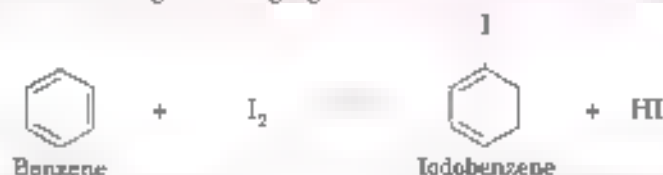


The *ortho*- and *para*-isomers can be easily separated due to large difference in their melting points.

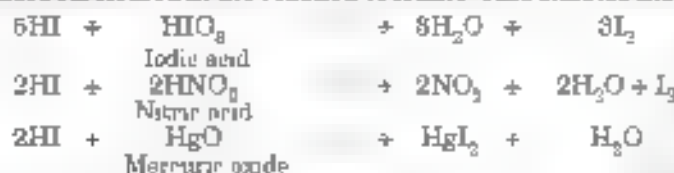
Bromo compounds can be prepared in a similar way by reacting with Br_2 in the presence of FeBr_3 .

The reaction with **fluorine** is violent and cannot be controlled. Therefore, fluoroarene cannot be prepared by direct fluorination of aromatic hydrocarbon.

Iodoarenes are also difficult to prepare and these cannot be prepared by direct iodination because the reaction is reversible and HI produced is a strong reducing agent to reduce iodobenzene back to benzene.

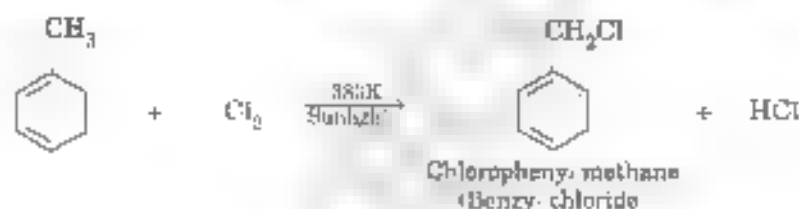


Therefore, the reaction is carried out in the presence of an oxidising agent like iodic acid or nitric acid or mercuric oxide, etc which oxidises HI formed in the reaction to iodine. This enables the reaction to proceed in the forward direction.

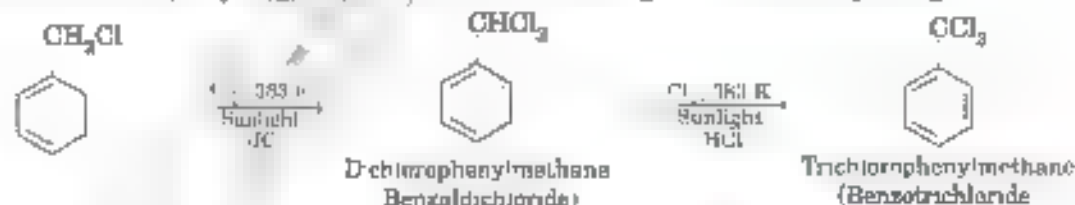


(b) Side chain halogenation – Preparation of aralkyls.

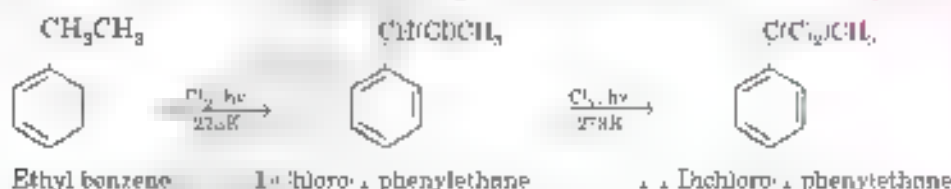
Side chain substituted aryl halides or aralkyl halides are prepared by direct halogenation of a suitable hydrocarbon. For example, when chlorine gas is passed through toluene in the presence of sunlight substitution takes place in the side chain.



If Cl_2 is passed in excess, the other two hydrogen atoms of side chain also get substituted by halogen atoms.



When the side chain is larger than the methyl group, the side chain halogenation occurs preferentially at the benzylic carbon i.e. carbon atom next to the benzene ring. Therefore, it is also called **benzylic halogenation**.



REMEMBER

Side chain halogenation occurs preferentially at the benzylic carbon.

Instead of Cl_2 , SO_2Cl_2 or SOCl_2 at 475K in the presence of light and traces of peroxide may also be used for side chain halogenation of arenes.



REMEMBER

The side chain halogenation like halogenation of alkanes is a free radical substitution reaction. This is unlike nuclear halogenation which occurs through the intermediate formation of carbocations.

2. From diazonium salts

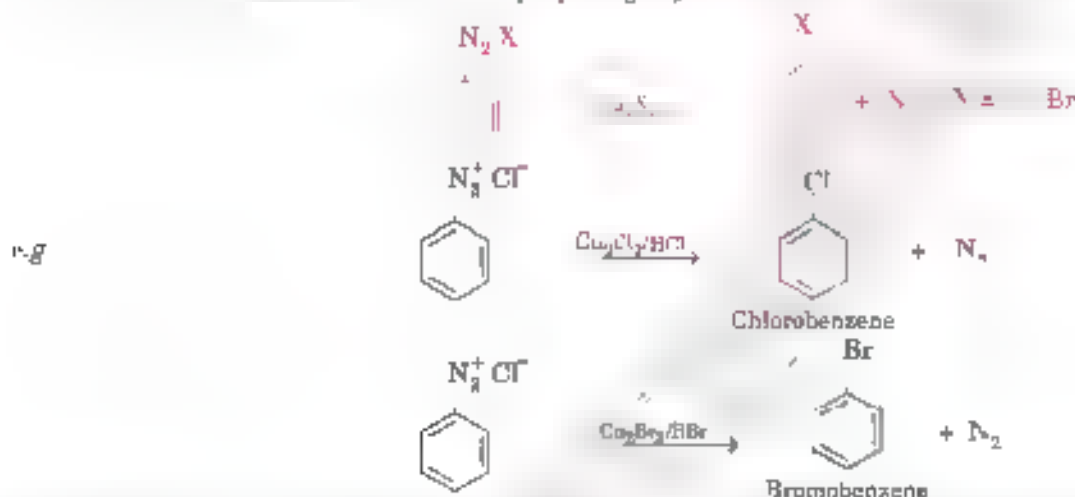
(i) By Sandmeyer reaction.

Chloro and bromoarenes are prepared by treating a freshly prepared diazonium salt solution with cuprous chloride or cuprous bromide dissolved in corresponding halogen acids. This reaction is called **Sandmeyer reaction**.

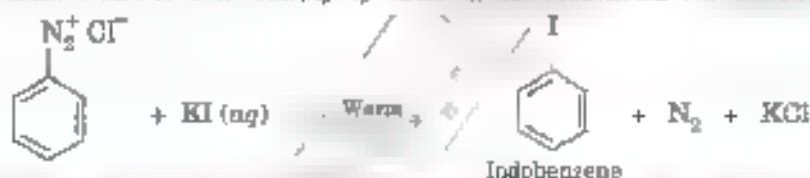
The benzene diazonium salts required for this purpose are prepared by treating *ice-cold* solution of aniline in excess of dilute HCl with an aqueous solution of sodium nitrite at low temperature, 273–278 K (0–5°C). The reaction is known as **diazotisation reaction**.



The benzene diazonium salt is used for preparing aryl halides as

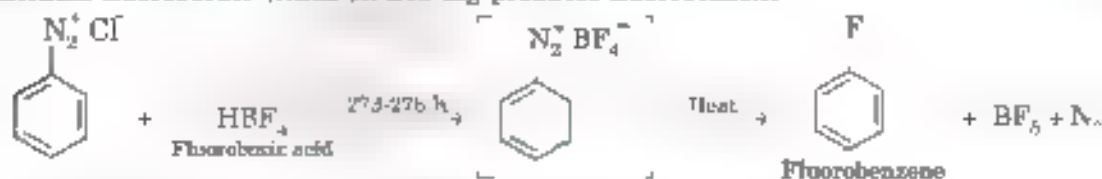


However for preparing **iodoarenes**, replacement of the diazonium group by iodine does not require the presence of cuprous halides and is done simply by shaking the diazonium salt solution with aqueous KI solution.



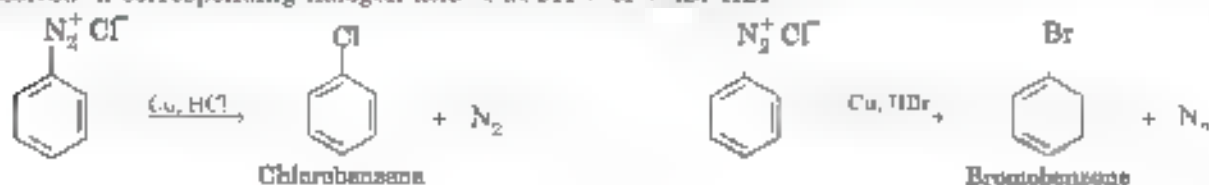
This is usually the best method for introducing iodine into benzene ring.

Fluoroarenes are prepared by treating benzene diazonium chloride with fluoroboric acid. This reaction produces diazonium fluoroborate which on heating produces fluorobenzene.



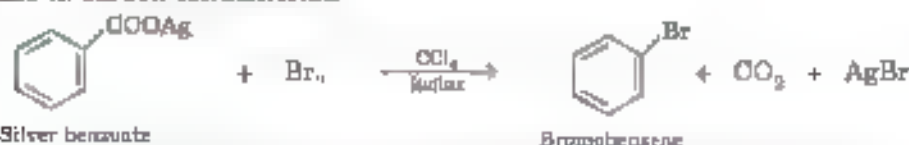
The reaction is called **Balz-Schiemann reaction**.

(ii) By Gattermann reaction. Haloarenes, particularly chloroarenes and bromoarenes are prepared by **Gattermann reaction** which is a modification of Sandmeyer reaction. The Sandmeyer reaction has been modified by using copper powder in the presence of corresponding halogen acids, HCl or HBr in place of cuprous halides dissolved in corresponding halogen acids, CuCl/HCl or CuBr/HBr.



3. From silver salt of aromatic acids + Hunsdiecker reaction

Like alkyl bromides, aryl bromides can also be prepared by refluxing the silver salt of aromatic acids with bromine in carbon tetrachloride.

**4. Commercial preparation of chlorobenzene - Raschig process**

Chlorobenzene is prepared commercially by passing a mixture of benzene vapours, air and hydrogen chloride over heated cupric chloride

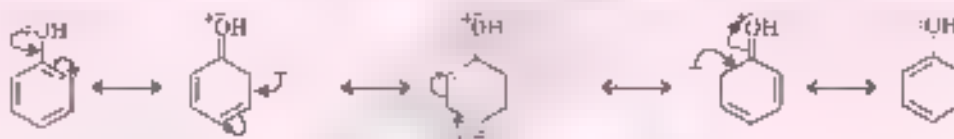


This is **Raschig process**.

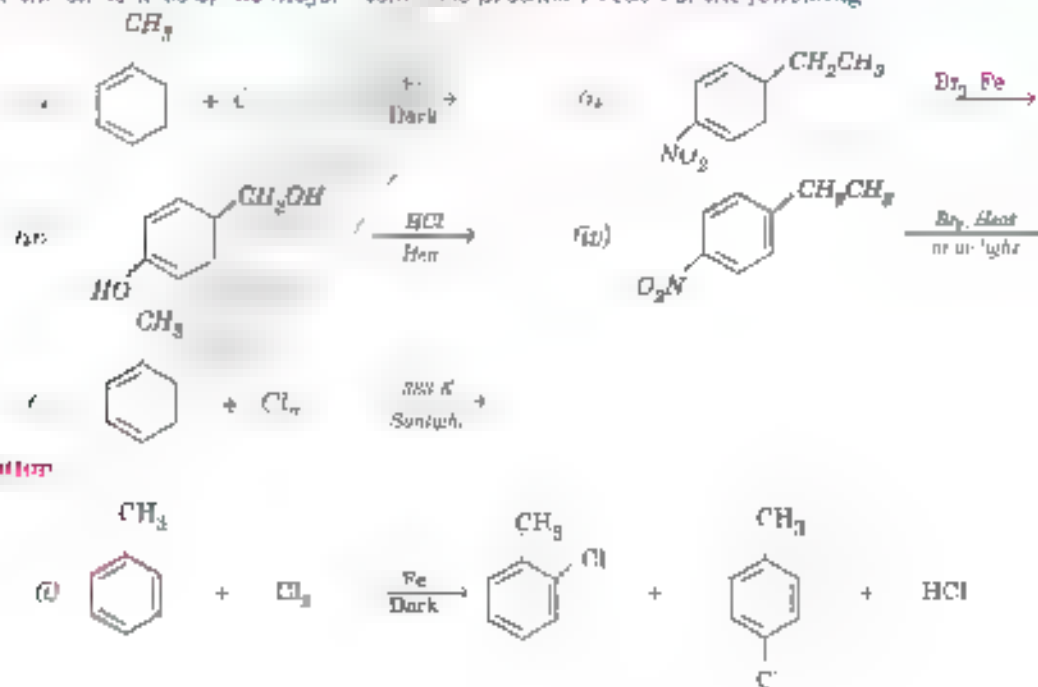
R U Curious...

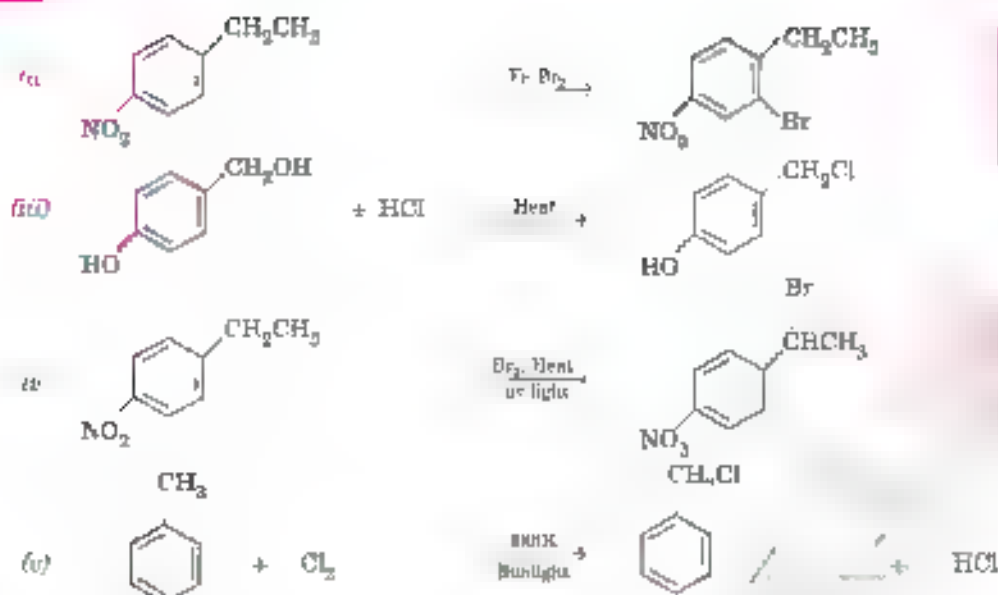
□ Haloalkanes can be easily prepared from alcohols by replacement of the -OH group by the halogen atom. Why cannot we prepare haloarenes from phenol?

► Haloarenes cannot be prepared from phenol as alkyl halide from alcohols because it is difficult to replace the -OH group of phenol by a halogen atom. This is due to resonance in phenol. Due to resonance in phenol, the carbon-oxygen bond in phenols has partial double bond character and is therefore, stronger than carbon-oxygen single bond in alcohols. As a result, the cleavage of carbon-oxygen bond in phenols is difficult under ordinary conditions.

**SOLVED EXAMPLES****□ Example 10**

Draw the structures of the major monosubstituted products in each of the following



**HELP**

A NO_2 group is a m -directing and NO_2 group is m -directing

HELP

Side chain halogenation occurs preferentially at the benzylic carbon.

PHYSICAL PROPERTIES OF HALOALKANES

The important physical properties of haloalkanes are

1. Physical state and smell. Haloalkanes in general are colourless (when pure), sweet-smelling liquids. Bromides and particularly iodides develop colour when exposed to light. However, the lower members like methyl chloride, methyl bromide and ethyl chloride and some chloro fluoromethanes are colourless gases at room temperature. Higher members are liquids or solids.

2. Solubility. Although haloalkanes are polar in nature, yet they are practically very slightly soluble in water. In order for a haloalkane to dissolve in water, energy is required to overcome the attractions between the haloalkane molecules and break the hydrogen bonds between water molecules. However, haloalkanes are not able to form hydrogen bonds with water and therefore, less energy is released, when new attractions are set up between the haloalkane and the water molecules because these are not as strong as the original hydrogen bonds in water molecules. As a result, solubility of haloalkanes in water is low. However, chloro, bromo and iodo derivatives are soluble in organic solvents such as alcohol, ether, benzene, etc. because new intermolecular forces between haloalkanes and solvent molecules have much the same strength as the ones being broken in the separate haloalkane and solvent molecules.

3. Density. Simple fluoro and chloroalkanes are lighter than water while bromides and polychloro derivatives are heavier than water. The densities increase in the order

fluoride < chloride < bromide < iodide.

	$\text{C}_2\text{H}_5\text{F}$	$\text{C}_2\text{H}_5\text{Cl}$	$\text{C}_2\text{H}_5\text{Br}$	$\text{C}_2\text{H}_5\text{I}$
Density (g mL^{-1})	0.890	1.280	1.335	1.747

With increasing size of the alkyl group, the densities of the alkyl halides go on decreasing

	CH_3I	$\text{CH}_3\text{CH}_2\text{I}$	$\text{C}_3\text{H}_7\text{I}$	$\text{C}_4\text{H}_9\text{I}$
Density g mL^{-1}	2.279	1.993	1.747	1.617

The density also increases with increasing number and atomic mass of the halogen

	CH_2Cl_2	CHCl_3	CCl_4
Density (g mL^{-1})	1.336	1.489	1.595

4. Melting and Boiling points. Molecules of organic halogen compounds are generally polar. Due to the polarity as well as higher molecular mass as compared to the parent hydrocarbon, the intermolecular forces of attraction (dipole-dipole and van der Waals) between the molecules are stronger in halogen derivatives of alkanes. As a result, melting and boiling points of chlorides, bromides and iodides are considerably higher than those of the parent hydrocarbon of comparable molecular mass.

Amongst themselves, the following trends are observed

For the same alkyl group the boiling points of alkyl chlorides, bromides and iodides follow the order $\text{RI} > \text{RBr} > \text{RCl} > \text{RF}$ where R is an alkyl group. This is because with the increase in the size of the halogen, the magnitude of van der Waals forces increases and consequently, the boiling points increase as shown below.

Haloalkane	CH_3F	CH_3Cl	CH_3Br	CH_3I	CH_4
b.p. (K)	104.0	248.8	278.0	315.4	112

In general, the boiling points of chloro, bromo and iodo compounds increase with increase in the number of halogen atoms.

Haloalkane	CH_3Cl	CH_2Cl_2	CHCl_3	CCl_4
b.p. (K)	249	313	334	350

iii. For the same halogen atom, the boiling points of haloalkanes increase with increase in the size of alkyl groups.

Haloalkane	CH_3Cl	$\text{CH}_3\text{CH}_2\text{Cl}$	$\text{CH}_3\text{CH}_2\text{CH}_2\text{Cl}$	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{Cl}$
b.p. (K)	248.8	285.5	320.0	351.5

iv. For isomeric alkyl halides, the boiling points decrease with branching. This is because branching of the chain makes the molecule more compact and, therefore, decreases the surface area. Due to decrease in surface area, the magnitude of van der Waals forces of attraction decreases and consequently the boiling points of the branched chain compound is less than that of the straight chain compounds. For example,

Haloalkane	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{Br}$	$\text{CH}_3\text{CH}(\text{CH}_3)\text{CH}_2\text{Br}$	$\text{CH}_3\text{CH}_2\text{CH}(\text{CH}_3)\text{Br}$	$\text{CH}_3\text{C}(\text{CH}_3)_2\text{CH}_2\text{Br}$
	α -Butyl bromide	Isobutyl bromide	sec-Butyl bromide	tert-Butyl bromide
b.p. (K)	375	364	364	348
Haloalkane	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{Cl}$	$\text{CH}_3\text{CH}(\text{CH}_3)\text{CH}_2\text{Cl}$	$\text{CH}_3\text{CH}_2\text{CH}(\text{CH}_3)\text{Cl}$	$\text{CH}_3\text{C}(\text{CH}_3)_2\text{CH}_2\text{Cl}$
	α -Butyl chloride	isobutyl chloride	sec-Butyl chloride	tert-Butyl chloride
b.p. (K)	351.5	343	341	334

The pattern of variation of boiling points of different alkyl halides is shown in Fig. 1.

5. Inflammable nature. Halogen compounds are less inflammable than hydrocarbons. The inflammability decreases with increasing halogen content. Interestingly, carbon tetrachloride is used as a fire extinguisher under the name **pyrene**.

Since organic halogen compounds are good solvents for oils and fats and also do not catch fire readily. For example, polychloro compounds such as CCl_4 and CHCl_3 have been widely used as solvents for dry cleaning. Carbon tetrachloride is used as a fire extinguisher under the name **pyrene**.

6. Polarity and Dipole moment. The carbon-halogen bond in haloalkanes is polar because of electronegativity difference between carbon and the halogen. As we move from F to I, the electronegativity of the halogen decreases.

	F	Cl	Br	I
Electronegativity	4.0	3.0	2.8	2.5

Therefore, the polarity of the carbon-halogen C-X bond and hence the dipole moment of the haloalkane should also decrease accordingly. However, the dipole moment decreases from Cl to Br to I, but dipole moment of CH_3F is slightly lower than that of CH_3Cl .

CH_3F	CH_3Cl	CH_3Br	CH_3I
1.847 D	1.880 D	1.830 D	1.636 D

The lower dipole moment of CH_3F than CH_3Cl is due to the small size of fluorine. Although the magnitude of -ve charge on F atom is much larger than that on the Cl atom, due to small size of F atom as compared to Cl atom, the C-F bond distance is so small that the product of charge and distance i.e. dipole moment of CH_3F comes out to be slightly lower than that of CH_3Cl .

	C-F	C-Cl	C-Br	C-I
Bond length	139 pm	178 pm	193 pm	214 pm

PHYSICAL PROPERTIES OF HALOARENES

The important physical properties of haloarenes or aryl halides are

- These are generally colourless liquids or crystalline solids.
- The aryl halides are heavier than water. These are *insoluble in water but soluble in organic solvents*.

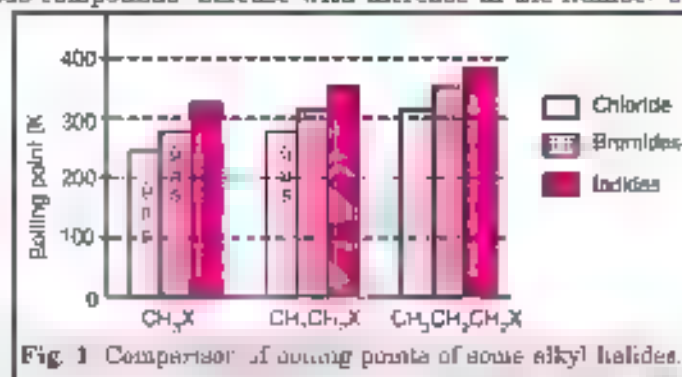
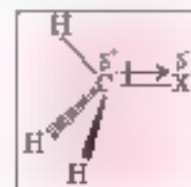



Fig. 1 Comparison of boiling points of some alkyl halides.



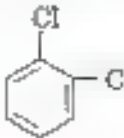
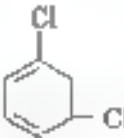

3. These are heavier than water.
 4. The melting and boiling points of aryl halides are nearly the same as those of alkyl halides containing the same number of carbon atoms. The boiling points of monohalogen derivatives of benzene are in the order
 $\text{iodo} > \text{bromo} > \text{chloro} > \text{fluoro}$

	F	Cl	Br	I
				
b.p. (K)	353	358	429	467

This trend is same as for alkyl halides.

For the same halogen atom the melting and boiling points increase as the size of the aryl group increases.

The boiling points of isomeric dihalobenzenes are nearly the same but their melting points are quite different as shown below

			
	ortho	meta	para
b.p.	453 K	446 K	448 K
m.p.	356 K	248 K	355 K

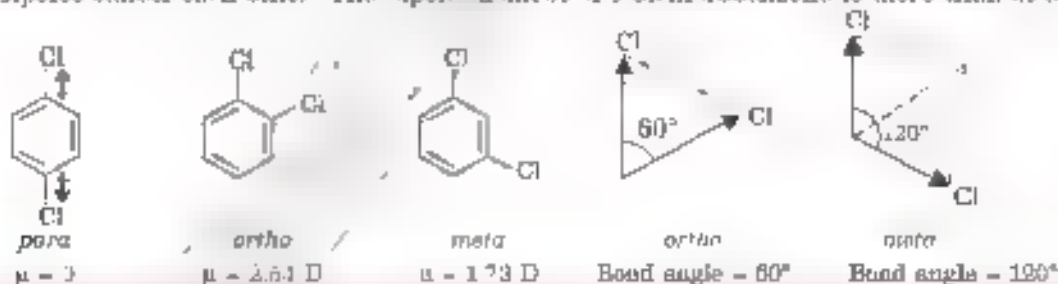
Generally the melting point of para isomer is quite higher than that of ortho or meta isomers. This is due to the fact that it has symmetrical structure and therefore its molecules can easily pack closely in the crystal lattice. As a result, intermolecular forces of attraction are stronger and therefore greater energy is required to break its lattice and it melts at higher temperature.

5. Fluorobenzene, chlorobenzene and bromobenzene have lower dipole moments than the corresponding methyl halides.

$\text{C}_6\text{H}_5\text{F}$	$\text{C}_6\text{H}_5\text{Cl}$	$\text{C}_6\text{H}_5\text{Br}$	$\text{C}_6\text{H}_5\text{I}$
1.60 D	1.69 D	1.70 D	1.70 D

The lowest dipole moment of fluorobenzene is probably due to small size of F atom.

Amongst isomeric dichlorobenzenes, the *p*-isomer has zero dipole moment because it is symmetrical and two equal and opposite dipoles cancel each other. The dipole moment of *o*-dichlorobenzene is more than *m*-dichlorobenzene.



The dipole moment of the *o*- and *m* isomer decreases as the bond angle between the two halogen atoms increases in accordance with the law of parallelogram of forces. According to the law of parallelogram of forces, the resultant dipole moment is given as

$$\mu = \sqrt{\mu_1^2 + \mu_2^2 + 2\mu_1\mu_2 \cos \theta}$$

where μ_1 and μ_2 are the dipole moments of C-X bonds and $\mu_1 = \mu_2$ and $\cos 60^\circ = 0.5$, $\cos 120^\circ = -0.5$

$$\mu(\text{ortho}) = \sqrt{\mu_1^2 + \mu_2^2 + 2 \times 0.5\mu_1\mu_2} \quad \text{and} \quad \mu(\text{meta}) = \sqrt{\mu_1^2 + \mu_2^2 - 2 \times 0.5\mu_1\mu_2}$$

Thus, the *o*-isomer with a bond angle of 60° between the two Cl atoms has higher dipole moment while *m*-isomer with a bond angle of 120° between the two Cl atoms will have lower dipole moment.

NATURE OF C-X BOND

The carbon-halogen bond in alkyl halides results from the overlap of a carbon sp^3 hybrid orbital with an orbital of halogen atom. Therefore, alkyl halides have tetrahedral geometry with $\text{H}-\text{C}-\text{X}$ bond angles nearly 109° . As the size of the halogen atom increases on going down the group, the bond lengths of haloalkanes increase accordingly and the bond dissociation enthalpies of C-X bonds decrease. Table 2. As we know, halogens are more electronegative

than carbon. Therefore, C—X bond is polar with the carbon having slight positive charge (δ^+) and halogen atom bearing a slight negative charge (δ^-). As a result, the C—X bond is polar.



The polarity of the C—X bond decreases with decrease in electronegativity of halogen atom. As a result, dipole moment decreases as given in Table 2.

Table 2. Comparison of bond length, bond energy and dipole moment of halomethanes.

Halomethane	Bond length (pm)	Bond enthalpy (kJ mol ⁻¹)	Dipole moment (D)
CH ₃ F	139	452	1.947
CH ₃ Cl	178	351	1.860
CH ₃ Br	193	298	1.830
CH ₃ I	214	234	1.636

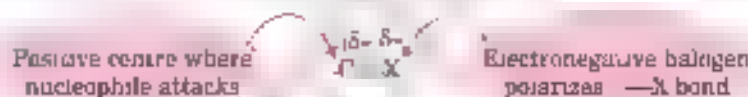
CHEMICAL PROPERTIES OF HALOALKANES

Haloalkanes are one of the most reactive classes of organic compounds. These can be used for the preparation of a large variety of useful organic compounds. Therefore *alkyl halides* are regarded as **synthetic tools** in the hands of a chemist. Some of the reactions of alkyl halides are given below.

- A. Nucleophilic substitution reactions B. Elimination reactions
C. Reactions with metals D. Reduction

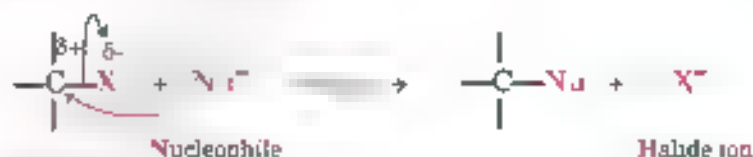
A. Nucleophilic Substitution Reactions

In haloalkanes, the carbon is bonded to a halogen atom (X = F, Cl, Br, I), which is more electronegative than carbon. Consequently, the C—X bond is polar in nature. As a result, carbon gets partial positive charge (δ^+) and the halogen atom gets partial negative charge (δ^-). The polar nature of alkyl halides makes them highly reactive molecules.



The presence of partial positive charge on the carbon atom makes it susceptible to attack by electron rich groups called **nucleophiles**. When a nucleophile stronger than the halide ion approaches the positively charged carbon atom of an alkyl halide, the halogen atom along with its bonding electron pair gets displaced and a new bond with the carbon and the nucleophile is formed.

These reactions in which a stronger nucleophile displaces a weaker nucleophile are called **nucleophilic substitution reactions**.



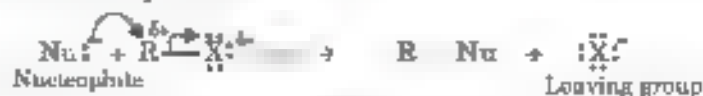
There are two types of nucleophiles which participate in substitution reactions of alkyl halides. These are

a. Negatively charged species OH^- , CN^- , R_3O^- , RCO_2^- , SH^- , R_3C^-

b. Neutral species with at least one lone pair



Therefore, nucleophilic substitution of a haloalkane is described by either of two general reactions. Negative nucleophile gives a neutral product.



Neutral nucleophile gives positively charged product (as a salt).



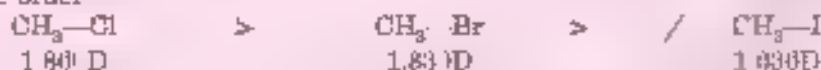
In these reactions, the atom or group of atoms which loses its bond to carbon and takes on an additional pair of electrons is called **leaving group**. Halide ions are good leaving groups. Better the leaving group, the faster is the nucleophilic substitution reaction. Among the alkyl halides, the leaving group ability increases along the series from fluoride to iodide as



Thus, iodide is the best leaving group and therefore, iodoalkanes undergo nucleophilic substitution reactions at the fastest rate. On the other hand, fluoride ion is the poorest leaving group and therefore, fluoroalkanes are least reactive.

Order of Reactivity of Haloalkanes

The reactivity of haloalkanes is due to the polar nature of C—X bond. The polarity of the bond depends upon the electronegativity difference between the carbon and the halogen atom. The polarity of the C—X bond in methyl halides decreases in the order



Therefore, the expected order of reactivity of haloalkane is



However, the actual order of reactivity of haloalkanes is just the reverse



This order is due to the bond dissociation enthalpy, i.e. the energy required to break the C—X bond. Lesser the bond dissociation energy, more will be the reactivity of the haloalkane. The bond dissociation energies of C—X (kJ mol⁻¹) are

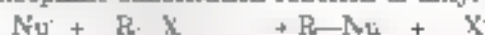
Bond	C—Cl	C—Br	C—I
Bond dissociation enthalpy kJ mol ⁻¹	320.4	284.5	213.4

Therefore, the C—I bond can easily be cleaved while the C—Cl bond is cleaved with difficulty. Fluoride forms the strongest bond with carbon among all the halogens and therefore, is least reactive. In fact, the C—F bond is so strong that organic fluorides do not undergo nucleophilic substitution reactions under ordinary conditions. This explains the order of reactivity of haloalkanes.

Reactions of Haloalkanes

Some important nucleophilic substitution reactions of haloalkanes with common nucleophiles are given in Table 3.

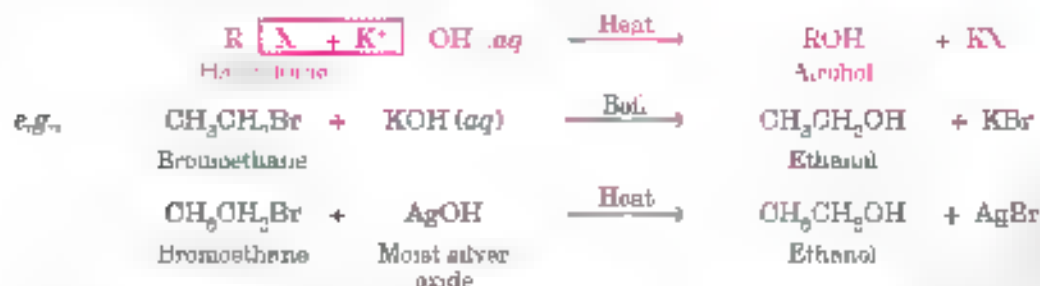
Table 3. Nucleophilic substitution reaction of alkyl halides, R—X



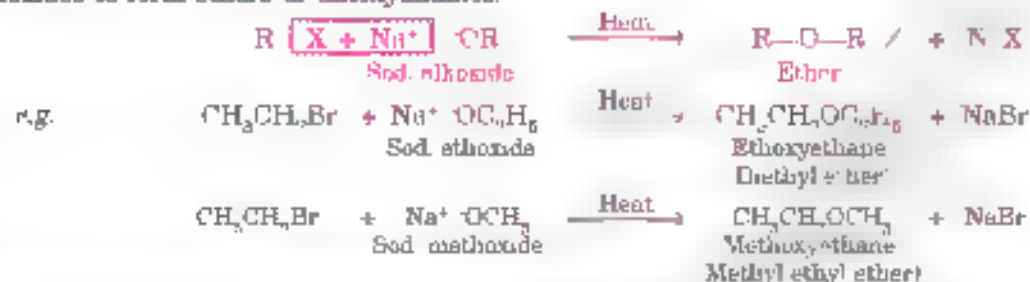
Reagent	Nucleophile (Nu ⁻)	Substitution product R—Nu	Class of main product
1. NaOH or KOH or moist Ag ⁺	OH^-	ROH	Alcohol
2. H ₂ O	H ₂ O	ROH	Alcohol
3. R'ONa	OR'	ROR'	Ether
4. NaI	I ⁻	R—I	Alkyl iodide
5. NH ₃	(NH ₃)	RNH ₂	Primary amine
6. R'NH ₂	R'N(H) ₂	RNHR'	Sec. amine
7. R'R''NH	R'R''N(H)	RNR'R''	Tert. amine
8. KCN	C≡N ⁻	RCN	Nitrile/cyanide
9. AgCN	Ag—C≡N:	RNC	Isocyanide/Isocyanide
10. KNO ₂	O=N—O ⁻	R—O—N=O	Alkyl nitrite
11. AgNO ₂	N ⁺ =O	R—NO ₂	Nitroalkane
12. R'COOAg	R'COO ⁻	R'COOR	Ester
13. NaHS	SH ⁻	RSR	Thioalcohol
14. R'SNa	SR'	RSR'	Thioether
15. NaN ₃	$\text{N}^-=\text{N}^+=\text{N}^-$	R—N=N=N	Azide
16. LiAlH ₄	H ⁻	RH	Hydrocarbon
17. R ⁺ —M ⁺	R ⁺	RR'	Alkane

These nucleophilic substitution reactions of haloalkanes are discussed below

1 Substitution by hydroxyl group (formation of alcohols). Haloalkanes react with boiling aqueous alkali (KOH) or moist silver oxide $\text{Ag}_2\text{O}/\text{H}_2\text{O}$ to form alcohols.



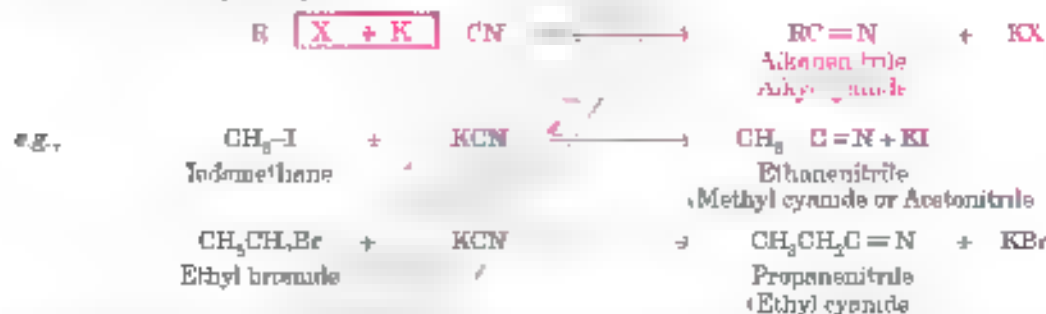
2. Substitution by alkoxy group (formation of ethers). Haloalkanes react with sodium or potassium alkoxides to form ethers or alkoxyalkanes.



This reaction is called **Williamson's synthesis** and is quite useful for preparing ethers. Haloalkanes can also be converted into ethers by heating with dry silver oxide



3. Substitution by cyano group (formation of cyanides or nitriles). Haloalkanes react with alcoholic solution of potassium cyanide KCN to give alkane nitriles or alkyl cyanides as the major products along with a small amount of alkyl isocyanides.

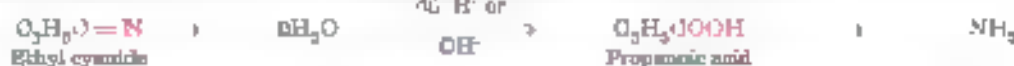


Alkyl cyanides can further be converted into acid amides, carboxylic acids and primary amines under different conditions. Therefore they are useful starting materials for these compounds.

Part (a) Hydrolysis: with conc. HCl or aqueous hydrogen peroxide (H_2O_2) gives acid amides



(b) Complete hydrolysis with dilute mineral acids or caustic alkali gives carboxylic acid.

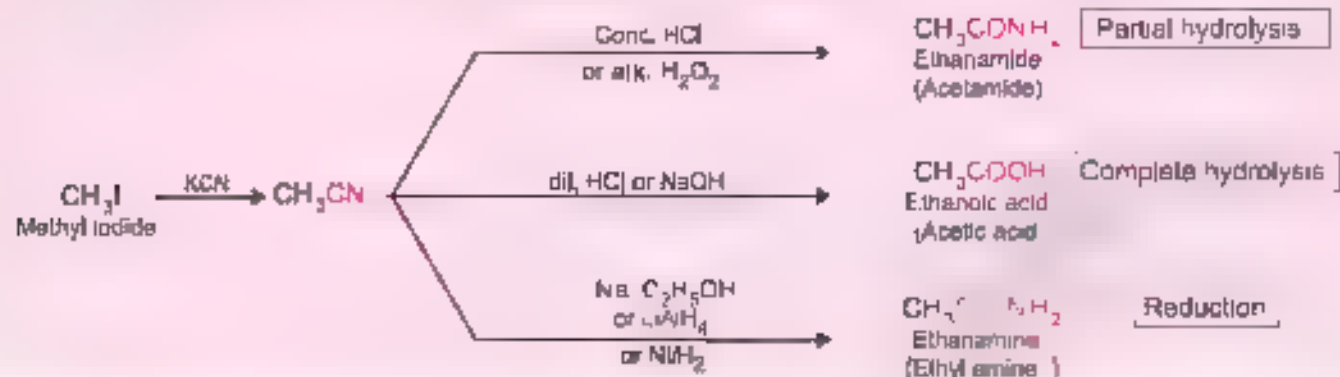


Reduction with sodium and alcohol (Mendius reaction) forms primary amine



The reduction can also be carried out with H_2 in the presence of Ni or Pt known as catalytic hydrogenation or with lithium aluminium hydride (LiAlH_4).

It may be noted that the reaction of haloalkanes with alcoholic KCN is very important because the product formed has one more carbon atom than the alkyl halide. Therefore, the reaction is a good method for increasing the length of the carbon chain by one carbon atom i.e. for ascending the homologous series.

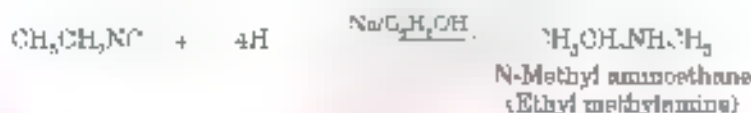


The formation of primary amines by reduction with nascent hydrogen, obtained by the action of sodium on alcohol is called **Wittmann reaction**.

4. Substitution by isocyanide group (formation of isocyanides). When haloalkane is treated with alcoholic silver cyanide AgCN, isocyanides are obtained. These are also called *isyl amines* and have extremely unpleasant smell.



Alkyl isocyanides on reduction with sodium or alcohol give secondary amines

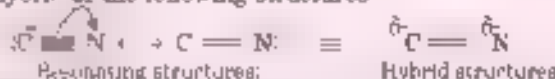


Be U Curious...



A curious question may come to our mind as to why haloalkanes give cyanides with KCN and isocyanides with AgCN as the product.

The cyanide ion is a resonance hybrid of the following structures

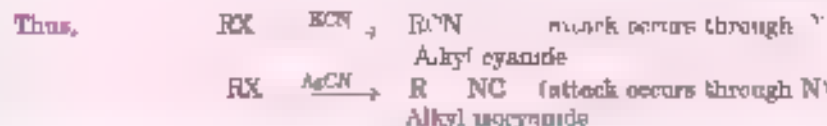
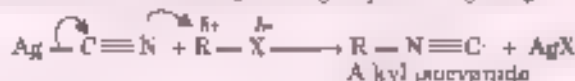


It is clear from the resonating structures that cyanide ion can attack the nucleophilic site through C as well as through N. Such a nucleophile which is capable of attacking through more than one atom (site) is called **ambident nucleophile**. Thus, CN⁻ behaves as an ambident nucleophile.

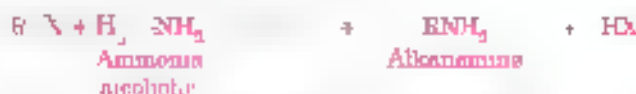
KCN or NaCN is predominantly ionic and therefore both C and N atoms are free to donate electron pair. Since C-N bond is relatively stronger than C-N bond, therefore, the attack occurs mostly through the carbon atom of the cyanide group forming **alkyl cyanides** as the major product.



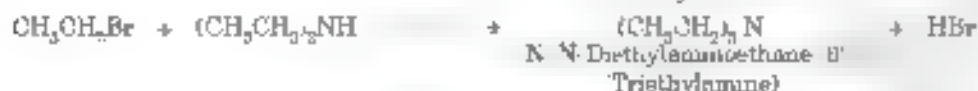
On the other hand, AgCN is predominantly covalent. Therefore, in this case only N-atom is free to donate electron pair and the attack mostly occurs through the N-atom of the cyanide group forming **alkyl isocyanides** as the major product.



5. **Substitution by amino group (formation of amines).** When haloalkane is heated with alcoholic ammonia solution in a sealed tube at 383 K, halogen is substituted by NH_2 group to form primary amine.



However, when haloalkane is in excess, one or both the hydrogen atoms of the amino alkane (primary amine) are replaced by alkyl groups and a mixture of primary, secondary and tertiary amines is formed.

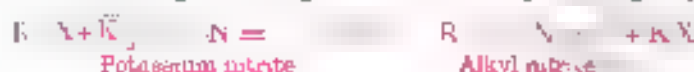


Tertiary amines so obtained can also combine with another molecule of alkyl halide to form quaternary ammonium salt.

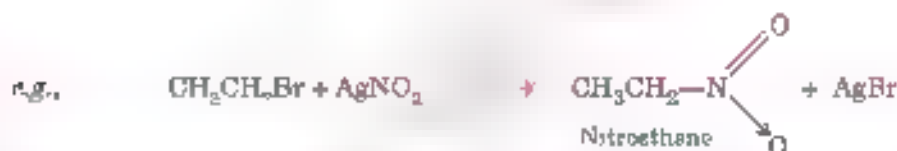


This reaction is called **Hoffmann ammonolysis reaction**.

6. **Substitution by nitrite group (formation of nitrite).** When a haloalkane is treated with sodium or potassium nitrite the halogen atom gets substituted by *nitrite group* $-\text{N}=\text{O}$ forming alkyl nitrites.

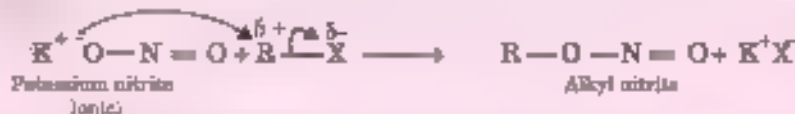


7. **Substitution by nitro group (formation of nitroalkanes).** When haloalkane is treated with silver nitrite AgNO_2 , the halogen atom is replaced by nitro group $-\text{NO}_2$ to give nitroalkanes.



Nitrite ion $^-\text{O}-\text{N}=\text{O}$ like cyanide ion is an ambident nucleophile because it has two sites (oxygen or nitrogen) through which it can attack the alkyl halide. *Attack through nitrogen gives nitro compounds and attack through oxygen gives nitrites.*

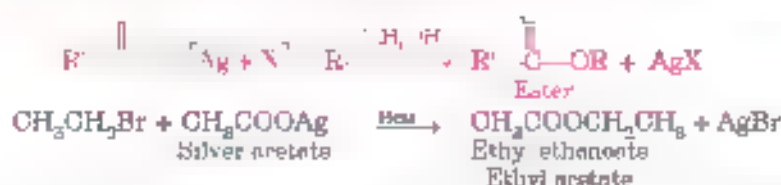
Alkali metal nitrites KNO_2 are ionic compounds and the bond between K^+ and $^-\text{O}-\text{N}=\text{O}$ is ionic and therefore the negative charge on oxygen is the attacking site. Hence, the attack of oxygen end on alkyl halide forms alkyl nitrites ($\text{R}-\text{O}-\text{N}=\text{O}$).



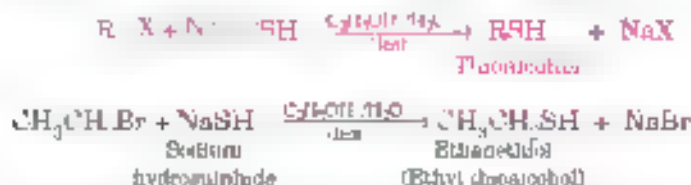
In the other hand, silver nitrite AgNO_2 is a covalent compound and the bond between Ag^+ and $^-\text{O}-\text{N}=\text{O}$ is covalent. Therefore, it does not have a negative charge on the oxygen atom. Hence, the nucleophilic attack occurs through the lone pair on nitrogen forming nitroalkanes ($\text{R}-\text{NO}_2$).



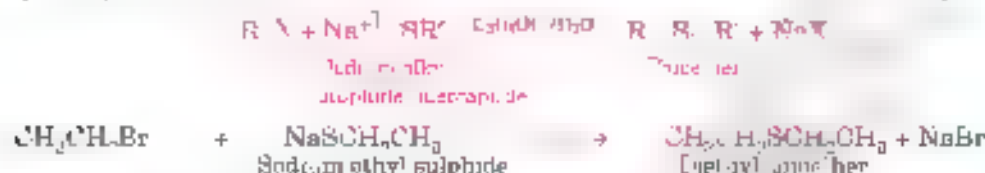
8. Substitution by carboxyl group (formation of esters): Haloalkanes form esters when heated with an ethanolic solution of silver salt of a fatty acid.



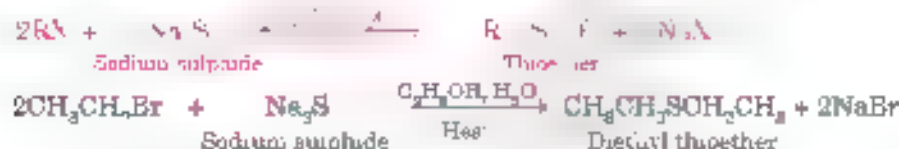
9. Substitution by hydrosulphide group (formation of thioalcohols): When haloalkane is treated with aqueous ethanolic solution of sodium or potassium hydrosulphide the halogen atom gets replaced by hydrosulphide ($-\text{SH}$) group to form thioalcohols or thiols.



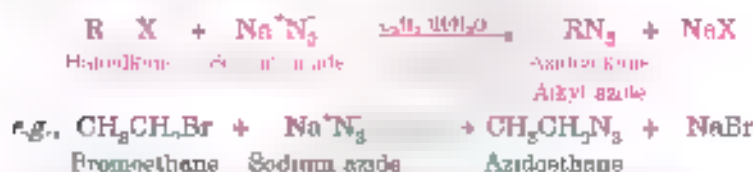
10. Substitution by alkyl sulphide group (formation of thioethers): By heating a mixture of haloalkanes with aqueous ethanolic sodium or potassium alkyl sulphides, thioethers are formed.



Thioethers are also formed by heating alkyl halide with sodium or potassium sulphide.



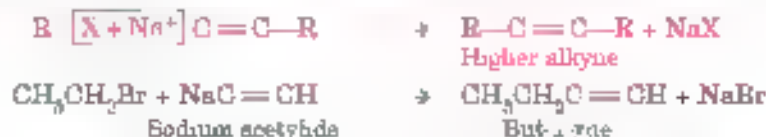
11. Substitution by azide group (formation of alkyl azides): When haloalkane is treated with sodium azide, they form alkyl azides or azidoalkanes.



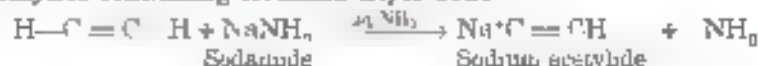
Alkyl azides are resonance hybrid of the following two resonance structures



12. Substitution by alkynyl group (formation of higher alkynes): When haloalkane is treated with sodium salt of alkynes (sodium alkynides), the halogen atom is replaced by alkynyl group ($-\text{C}\equiv\text{C}-$) to form higher alkynes.



The sodium alkynides needed for the above reaction are formed by the reaction of sodamide (or sodium in liquid NH_3) with alkynes containing terminal triple bond.



HELP

- The sulphur analogues of alcohols, $\text{R}-\text{SH}$ are called **thiols**. The ending *thiol* is added to alkane stem to give the name *alkane thiol*.
- The $-\text{SH}$ group is referred to as **mercapto** group.
- The sulphur analogues of ethers are called **thioethers** or **sulphides** as per alkyl ether nomenclature e.g. $\text{CH}_3\text{SCH}_2\text{CH}_3$, Ethyl methyl thioether or ethyl methyl sulphide.
- The $-\text{RS}$ group is named as **alkylthio** group and RS^- group is named as **alkyl thiolate** e.g. $\text{CH}_3\text{S}^- \text{Na}^+$ Sodium methyl thiolate.

Mechanism : Two types of Nucleophilic Substitution Reactions

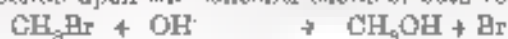
The nucleophilic substitution reactions of alkyl halides have been found to proceed in the following two types of mechanisms

1) Substitution nucleophilic bimolecular, S_N2

2) Substitution nucleophilic unimolecular, S_N1

(1) Substitution nucleophilic bimolecular, S_N2 reactions.

The reaction between methyl bromide CH_3Br and hydroxide ion (OH^-) to form methanol follows a second order kinetics i.e., rate depends upon the concentrations of both reactants alkyl halide and hydroxide ion.



The rate of the reaction may be expressed as

$$\text{Rate} = k[\text{CH}_3\text{Br}][\text{OH}^-]$$

In fact, methyl or primary alkyl halides follow this type of mechanism and it may be written as

$$\text{Rate} = k[\text{RX}][\text{OH}^-]$$

This reaction is also called **nucleophilic substitution bimolecular** because two molecules take part in determining the rate of the reaction. It is written as S_N2 short form for *substitution nucleophilic bimolecular*.

This type of reaction occurs in **single (concerted) step** through the formation of a transition state. In this mechanism, the nucleophile (OH^-) attacks the partially positively charged carbon atom of carbon halogen bond from the direction 180° away from the halogen atom, i.e. from the backside. This leads to a transition state with a partially formed $\text{C}-\text{OH}$ bond and a partially broken $\text{C}-\text{Br}$ bond. This process is said to be a one step reaction. In the transition state, the negative charge is shared by both the incoming nucleophile as well as outgoing bromide. Hydroxide has diminished negative charge because it has begun to share its electrons with carbon while bromine has developed partial negative charge because it has partly removed a pair of electrons from carbon. Therefore, both OH^- and Br^- have partial negative charge, i.e. δ^- . The remaining three bonds to carbon in the transition state adopt a planar arrangement. This arrangement may be described as the $\text{C}-\text{H}$ bonds are arranged like the spokes of a wheel with $\text{C}-\text{OH}$ and $\text{C}-\text{Br}$ bonds lying along the axle.

The transition state is unstable because carbon atom is simultaneously bonded to five atoms and therefore, changes to products in which bromide ion leaves forming a $\text{C}-\text{O}$ bond. This reaction is shown below



HELP

In these reactions, bond making occurs at the same time as bond breaking. Because the two events occur in concert, we call these reactions as **concerted reactions**.

As you have learnt in previous class, solid wedge represent the bond coming out of the paper, dashed line represents the bond going behind the paper and straight lines represent bonds in the plane of the paper.

In terms of models, the reaction path may be diagrammatically represented as given in Fig. 2

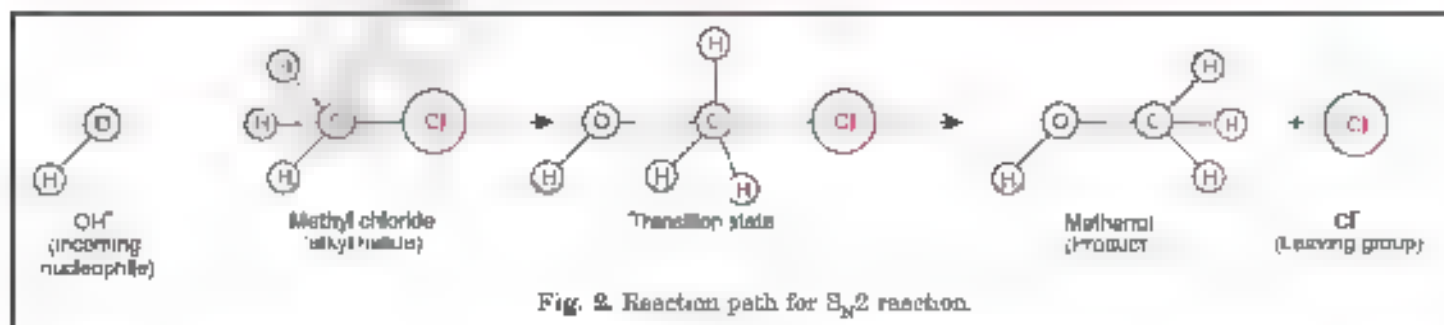


Fig. 2. Reaction path for S_N2 reaction.

It is clear from the above one step mechanism that the formation of transition state is rate determining step and therefore, the rate of the reaction depends upon the concentration of both alkyl halide and OH^- . Hence, it is a second order reaction or a bimolecular reaction.

It may be noted that as a general rule nucleophilic substitution occurs only when the group being displaced X is easily able to leave taking with it the electron pair of the $C-X$ bond. The relative ease at which it can be displaced or its **leaving group ability** depends upon its capacity to accommodate the negative charge. For the halogens the leaving group ability increases along the series from fluorine to iodine.



Route

Fund

Leaving group ability decreases

This, iodide is regarded as a 'good' leaving group while fluoride is regarded as a 'poor' leaving group.

Reactivity of alkyl halides towards S_N2 reaction

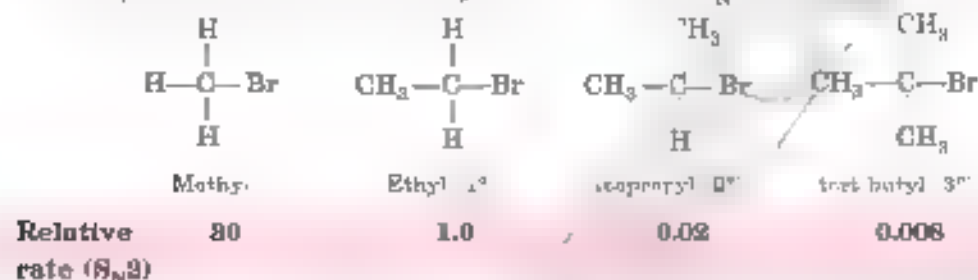
The reactivity of alkyl halides towards S_N2 mechanism has been found to be in the following order

Methyl halide > Primary halide > Secondary halide > Tertiary halide

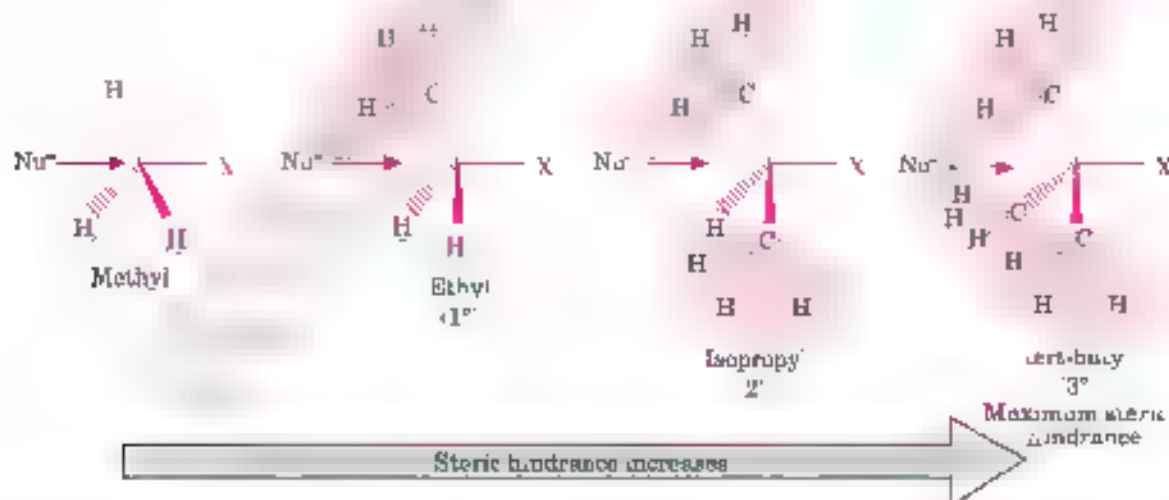
This can be easily explained on the basis of formation and stability of transition state in the reaction. Since the reaction requires the approach of the nucleophile to the carbon bearing the leaving group, the presence of bulky substituents on or near the carbon hinders the attack of nucleophiles and therefore slows the reaction. This interference of the bulky groups with a reaction is called **steric hindrance**. Therefore of the simple alkyl halides methyl halides react most rapidly in S_N2 reaction because there are only three small hydrogen atoms (least steric hindrance). On the other hand, tertiary alkyl halides are least reactive because of the presence of three bulky groups on carbon (maximum steric hindrance). Thus, the order of reactivity is



For example, the relative rate of alkyl halides towards S_N2 reaction has been found to be



The steric effects in S_N2 reaction are shown below

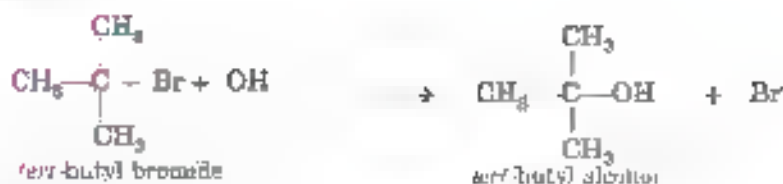


NOTE

It should be noted that neopentyl chloride a primary chloride reacts about 2500 times more slowly than isopropyl chloride a secondary chloride. This is due to an extremely bulky tert butyl group attached to the electrophilic carbon. A single tert butyl group hinders the backside approach of nucleophile even more than two methyl groups.

2. Substitution nucleophilic group-decylar S_N reactions

The reaction between *tert*-butyl bromide and hydroxide ion to form *tert*-butyl alcohol follows first order kinetics, i.e. the rate depends on the concentration of one reactant only. It has been observed that rate of reaction depends only on the concentration of alkyl halide.



The rate of reaction may be expressed as

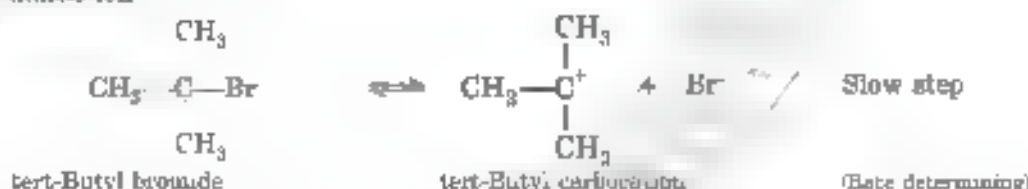
$$\text{Rate} = k_0 [\text{CH}_3)_3\text{CBr}]$$

$$\text{or simply, Rate} = k [\text{RX}]$$

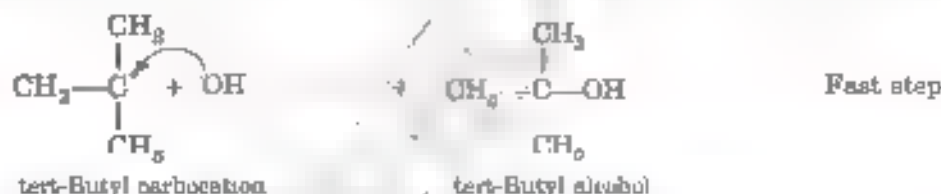
This reaction is called substitution nucleophilic unimolecular because only one molecule is involved in determining the rate of the reaction and is written as S_N1 reaction. Such type of reactions are generally carried out in polar protic solvents such as water, alcohol, acetic acid, etc.

The S_N1 mechanism occurs in two steps.

Step 1. Formation of carbocation. The polarised C—halogen bond C—Br undergoes slow cleavage to form a carbocation and a halide ion.



Step 2. Nucleophilic attack on carbocation. The carbocation is very reactive species. Therefore it readily reacts with a nucleophile, OH^- to form the product.



The first step is slow and reversible. It involves the cleavage of C—Br bond for which energy is obtained through solvation of bromide anion with the proton of the protic solvent. Since the slowest step is the rate determining step, the rate of reaction depends only on the concentration of tert-butyl bromide (alkyl halide). Hence, it is a **first order** or unimolecular reaction.

The S_N1 mechanism is facilitated by polar protic solvents such as water, alcohol or aqueous organic solvents. These solvents promote the ionisation step by solvating the ions by solvation.

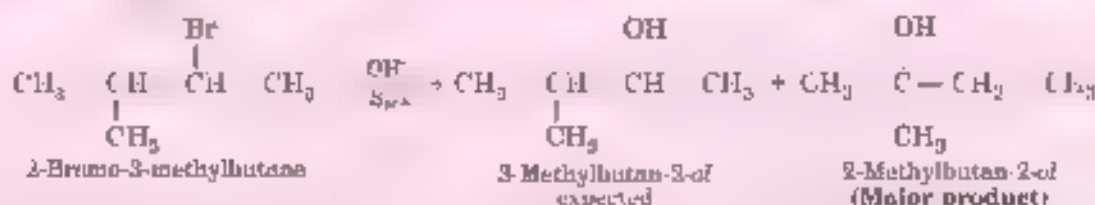
Carbocation Rearrangements : A unique property

Carbocation Rearrangements

The S_N1 reaction proceeds through the formation of a carbocation. The carbocations have the unique property of rearrangement. Carbocations rearrange if they become more stable as a result of rearrangement. Therefore, the products formed are different than expected products.

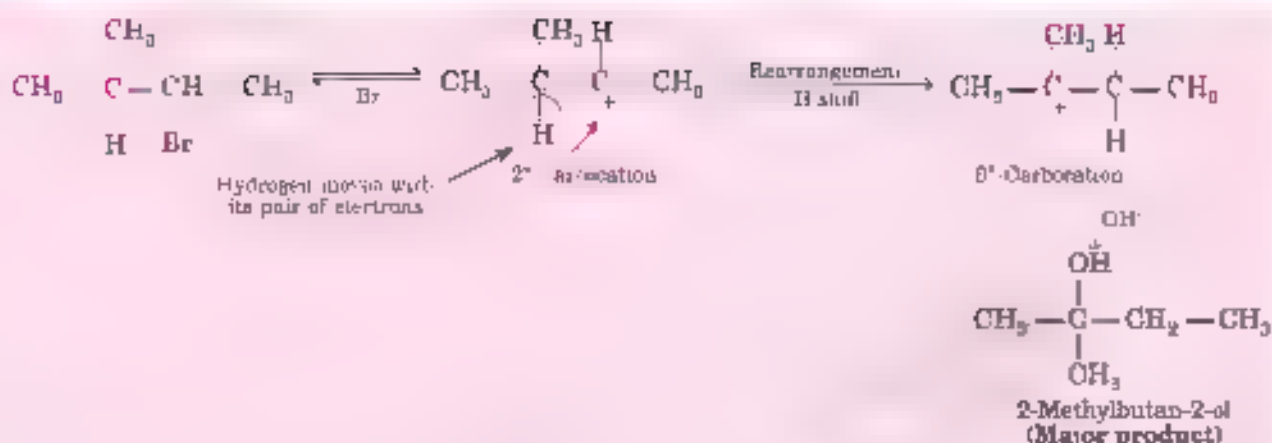
However, rearrangement does not occur in S_N2 reaction where no carbocation is formed and one step mechanism does not allow any rearrangement. Therefore, if the carbocation formed in an S_N1 reaction can rearrange, then S_N1 and S_N2 reactions of the same alkyl halide will give different products (constitutional isomers).

For example, the major product obtained when 2-bromo-3-methylbutane undergoes S_N1 reaction is different than expected.



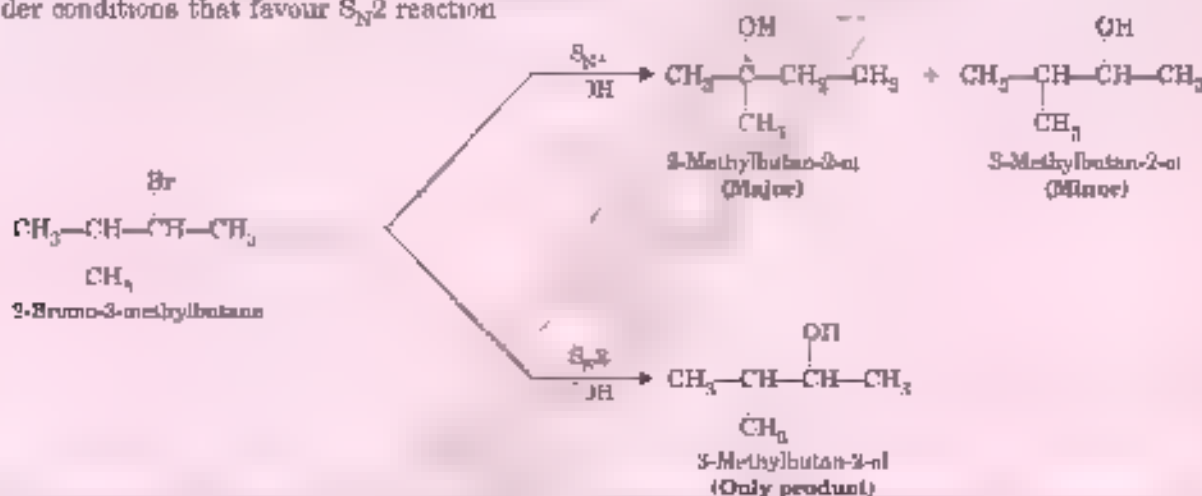
The major product results from the rearrangement of carbocation. The carbocation initially formed can rearrange to a more stable carbocation if the structure of a β -hydrogen group permits. This occurs either through a **hydride shift**

H or the movement of a hydrogen atom with its bonding pair of electrons or a **methyl shift** CH_3 the movement of a methyl group with its bonding pair of electrons. For example, the above reaction may be represented as

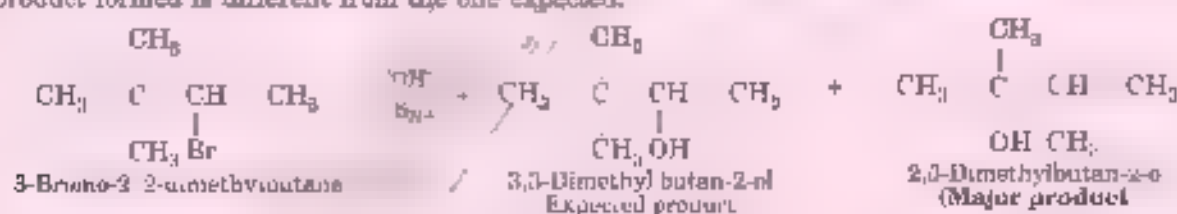


3° -carbocation rearranges to 3° -carbocation because 3° -carbocation is more stable than 2° -carbocation. Thus is called **1,2-hydride shift**.

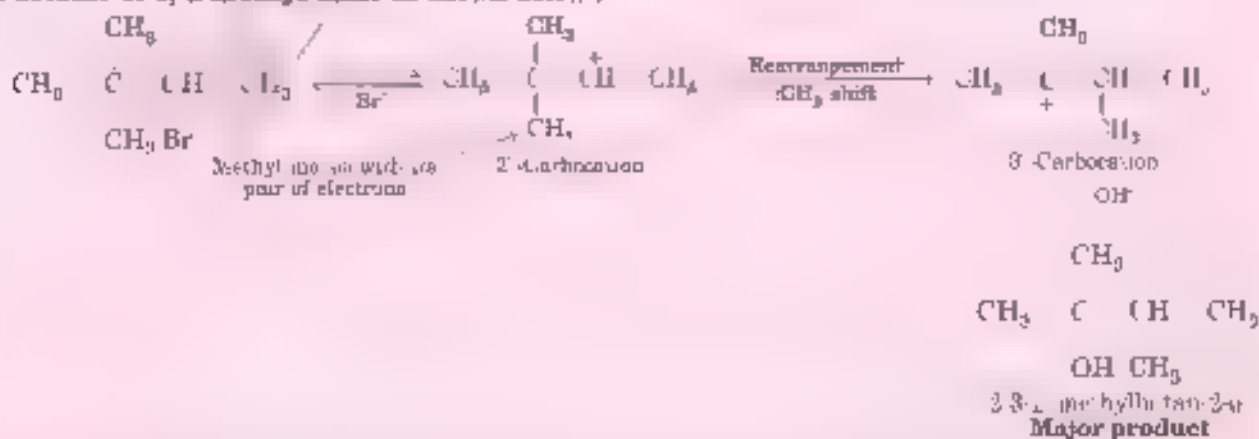
Thus the product formed when 2-bromo-3-methylbutane undergoes an $\text{S}_{\text{N}}1$ reaction is different from the product formed under conditions that favour $\text{S}_{\text{N}}2$ reaction.



Similarly when 3-bromo-2,2-dimethylbutane is treated with CH_3OH or under conditions that favour $\text{S}_{\text{N}}1$ reaction, the product formed is different from the one expected.



This is because of **1,2-methyl shift** as shown below,



The 2° carbocation rearranges to 3° carbocation because 3° carbocation is more stable than 2° carbocation. This is called **1,2-methyl shift**. Thus, if structure permits rearrangement of carbocations occurs in such a way that a less stable carbocation is converted into a more stable carbocation.

□ **Concluding note** When a reaction forms a carbocation intermediate, always check for the possibility of a carbocation rearrangement.

Reactivity of alkyl halides towards S_N1 reaction

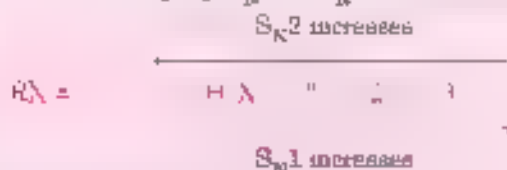
The order of reactivity depends upon the stability of carbocation in the first step. Greater the stability of the carbocation, greater will be its ease of formation from alkyl halide and hence faster will be the rate of the reaction. As we know 3° carbocation is most stable, therefore, the tert-alkyl halides will undergo S_N1 reaction very fast. The order of reactivity will be

tertiary alkyl halide > secondary alkyl halide > primary alkyl halide > methyl halide

For example, it has been observed that the reaction $\text{CH}_3)_3\text{CBr}$ with OH^- ion to give 2-methyl-2-propanol is about 1 million times as fast as the corresponding reaction of the methyl bromide to give methanol.

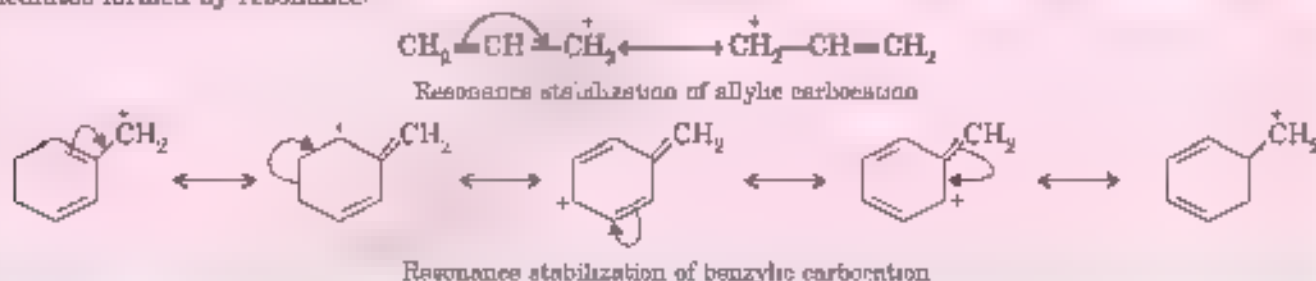
	$\text{CH}_3)_3\text{CBr}$	$(\text{CH}_3)_2\text{CHBr}$	$\text{CH}_3\text{CH}_2\text{Br}$	CH_3Br
Relative rate (S_N1)	1.2×10^6	12	1	1

Thus, the reactivity by S_N1 vs S_N2 follows as



Thus, the primary alkyl halides always react predominantly by S_N2 mechanism. In the other hand, the tertiary alkyl halides react predominantly by S_N1 mechanism. Secondary alkyl halides may react by either mechanism or by both the mechanisms without much preference depending upon the nature of the nucleophile and solvent.

It may be noted that primary allylic and primary benzylic halides show higher reactivity in S_N1 mechanism than other primary alkyl halides. This is because of the greater stabilization of the allylic and benzylic carbocation intermediates formed by resonance.



Some Basic Concepts about Optical Activity and Optical Isomerism

The stereochemistry plays a significant role in understanding the mechanisms of nucleophilic substitution reactions. For example, a S_N2 reaction proceeds with complete stereochemical inversion of configuration while a S_N1 reaction proceeds with **racemisation**.

To understand these concepts, let us learn about some basic stereochemical principles and the terms commonly used.

Plane Polarised Light and Optical Activity

A beam of ordinary light consists of electromagnetic waves vibrating in all planes perpendicular to the direction of light. When ordinary light is passed through a Nicol prism (a special type of prism made of crystaline calcium carbonate), the light emerging out of it, consists of rays vibrating in one plane only. Such a beam of light which consists of waves of light vibrating in one plane only is called plane polarised light. In the prism, the vibrations in all other planes except in one plane are cut off. The Nicol prism used to make ordinary light into plane polarised light is called **polariser**.



Optical activity

When the solutions of certain organic compounds, such as sugar, camphor, are placed in the path of a plane polarised light, they rotate the path of the plane polarised light either to the left or to the right. Not all the organic substances rotate the plane polarised light. The substances which rotate the plane polarised light are called **optically active substances**. The common examples are *lactic acid, tartaric acid, glucose, fructose, etc.* The substances which do not rotate the plane of the polarised light are called **optically inactive substances**.

This property of a substance to rotate the plane of polarised light towards right or towards left is called optical activity.

All optically active substances do not rotate the plane of polarised light in the same direction. Some rotate the plane of the polarised light to the right (clockwise) while some rotate it to the left (anti-clockwise). The direction and the magnitude of the rotation of plane of the polarised light by a substance is measured with the help of an instrument called **polarimeter** (Fig. 3).

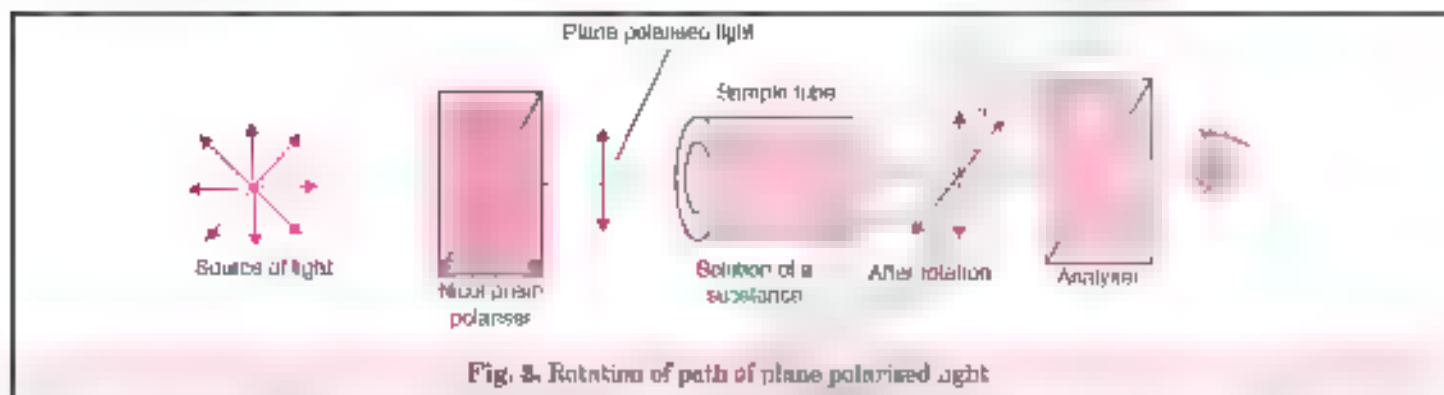


Fig. 3. Rotation of path of plane polarised light

The polarimeter consists of a light source, two nicol prisms and the sample tube to hold the substance. The prism placed near the source of light is called **polariser** while the other placed near the eye is called **analyser**.

The aqueous solution of the substance under investigation is placed in the sample tube placed between the polariser and the analyser. The polariser, sample tube and analyser are arranged in such a way that the light after passing through polariser, sample tube and the analyser reaches our eye. When the tube is empty, we observe that maximum amount of light reaches our eyes. If we rotate the analyser which is nearer to our eye, we observe that light gets dim and reaches a minimum when the lens is at right angles to its previous position. Let us adjust the lens so that a maximum amount of light reaches our eyes. Now place the aqueous solution of the substance in the sample tube and observe the effect on the light.

If the substance does not rotate the plane polarised light, it is said to be **optically inactive**.

If the substance rotates the plane polarised light, it is called **optically active substances**.

- A substance which rotates the plane of polarised light to the right is called **dextro-rotatory** (Latin *dexter* = right). Such compounds are designated as *d-* or by the sign (+).
- A substance which rotates the plane of polarised light towards the left is called **laevo-rotatory** (Latin, *laevus* = left). Such compounds are designated as *l-* or by the sign (-).

For example, lactic acid which is extracted from muscle tissues rotates light to the right and hence is known as **dextro-rotatory lactic acid** or (+) or *d*-lactic acid. On the other hand, 2-methylbutan-1-ol which is obtained as a by product of the fermentation of starch, **l-amylic alcohol** rotates the light to the left and is known as **laevo-rotatory 2-methylbutan-1-ol** or (-) or *l*-2-methylbutan-1-ol.

Currently dextro and laevo-rotatory rotations are represented by algebraic signs of (+) for dextro and (-) for laevo (instead of *d* and *l*).

Such (+) and (-) isomers of a compound are called **optical isomers** and the phenomenon is termed as **optical isomerism**.

Specific Rotation

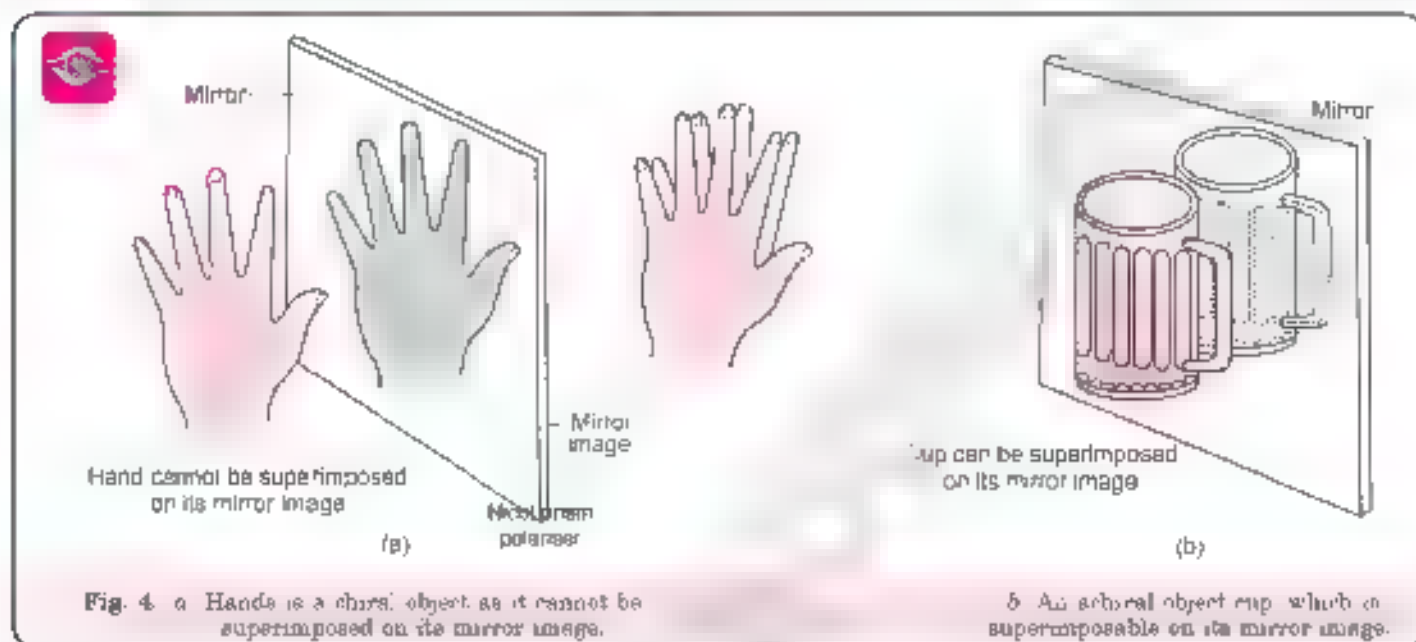
To express optical rotation data in a meaningful way so that comparison can be made, we have fix standard conditions. The optical rotation, thus observed is called **specific rotation**. It is defined as

the number of degrees of rotation observed by 1.0 g of sample in 1.00 mL of solution in a tube with path length 1.0 decimeter using a D light (589.3 nm wavelength) at a specified temperature.

While reporting specific rotation $[\alpha]$ the wavelength of the light used is given as subscript and the temperature in degrees Celsius as a superscript. It is also customary to designate the solvent and the concentration. For example, $[\alpha]_D^{25} = +2.25^\circ$ (c 0.50) ethanol means that α was measured at 25°C using D-line of sodium and the sample concentration was 0.50 g/mL in ethanol.

Molecular Asymmetry and Chirality of Objects and Molecules

In 1848, Louis Pasteur observed that crystals of certain substances such as sodium ammonium tartrate exist in two forms which are mirror images. This observation laid the foundation of modern stereochemistry. He demonstrated that



aqueous solution of both types of crystals showed optical rotation of equal magnitude for solution of same concentration, but opposite in direction. He attributed this difference in optical activity to the three dimensional arrangement of atoms called **configurations** in two types of crystals.

Dutch scientist, J. Van't Hoff and French scientist C. Le Bel, both independently in the same year (1874) pointed out that the four valencies of carbon atom are directed towards the corners of a regular tetrahedron and if all the atoms or groups attached to a carbon atom are different, then such a carbon atom is called **asymmetric carbon atom** or **stereocentre**. The molecule containing asymmetric carbon would lack symmetry and is called **asymmetric molecule**. This asymmetry of the molecule is responsible for optical activity in compounds. The symmetry and asymmetry are also observed in many day to day objects as discussed below.

All objects or molecules have mirror images.

An object or a molecule which is not superimposable on its mirror image is called chiral.

The most common example of a chiral object is human hand. If we hold our left hand in front of a mirror, the image looks like the right hand. If we try to superimpose left and right hands, both palms down, we observe that the hands cannot be superimposed.

Therefore, hands are chiral. Similarly, gloves, shoes, etc. are chiral objects. The word chiral (*ky-ral*) a word derived from the Greek word *cheir* which means hand, is used for those objects which have right-handed and left-handed forms. The general property of ~~handedness~~ handedness is called **chirality**. On the other hand, a cup, fork, glass tumbler, spoon, a sphere, a cube or a cone are identical with their mirror images. Therefore, these can be superimposed on their mirror images. Such objects which are superimposable on their mirror images are called **achiral**. Thus

- chiral object has non-superimposable mirror image
- achiral object has superimposable mirror image

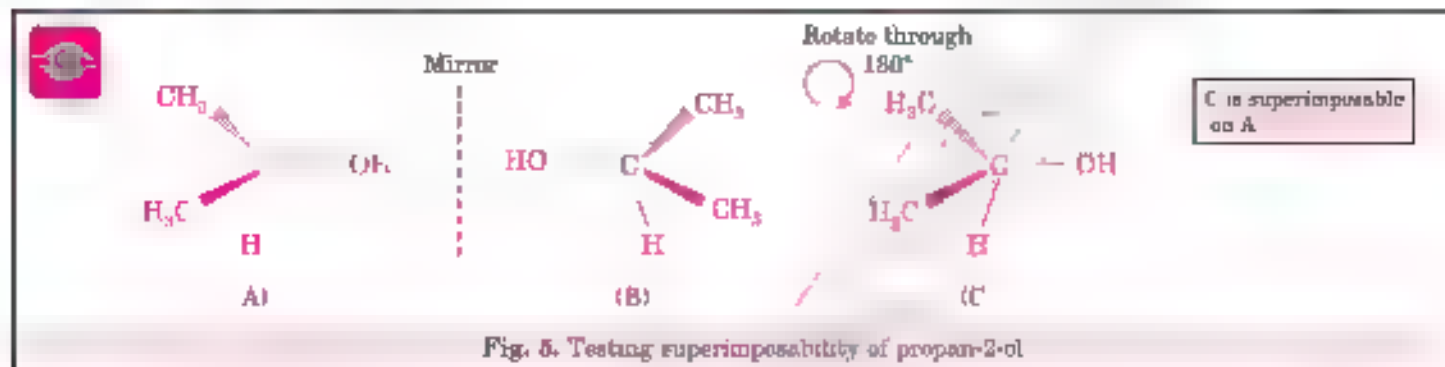
The same principle of right and left handedness can apply to organic molecules. Though all molecules have mirror images, not all molecules are superimposable on their mirror images, atom for atom. On the other hand, there are some molecules which cannot be superimposed on their mirror images.

The molecules which are not superimposable on their mirror images are called chiral molecules. The property of non-superimposability of a structure on its mirror image is called chirality.

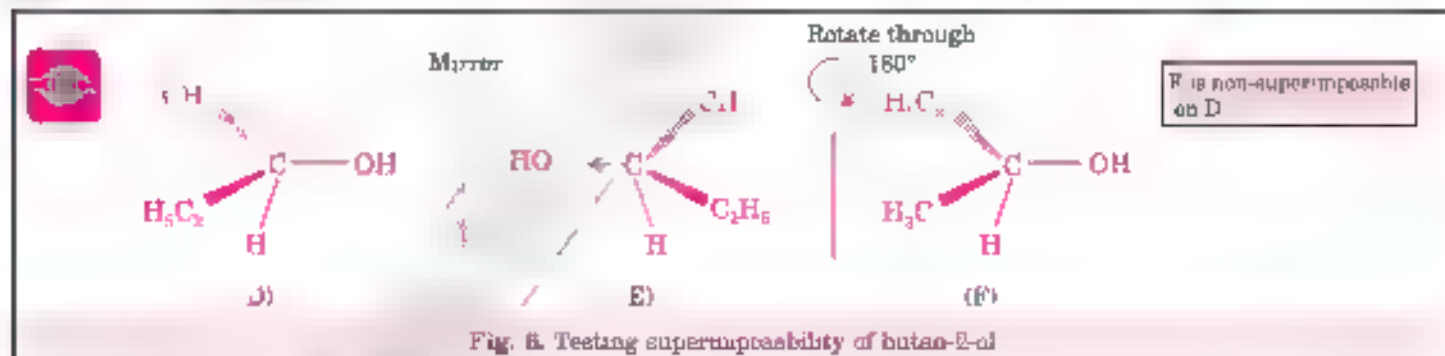
Similarly molecules which are superimposable on their mirror images are called **achiral molecules**. The study of structure of optically active substances reveals that all of them are chiral in nature. For example, organic molecules such as butan-2-ol, $\text{CH}_3\text{CH}(\text{OH})\text{CH}_2\text{CH}_3$, 2-chlorobutane $\text{CH}_3\text{CH}(\text{Cl})\text{CH}_2\text{CH}_3$, lactic acid $\text{CH}_3\text{CH}(\text{OH})\text{COOH}$ have chiral structures i.e. they form non-superimposable mirror images.

Let us test the superimposability of two simple molecules propan-2-ol and butan-2-ol. We do it manually and examine them by overlap procedure.

As is evident, propan-2-ol does not contain an asymmetric carbon, because all the four atoms or groups attached to the carbon are not different. Therefore, it is an **achiral molecule**. Let us confirm it by the superimposability test. The three dimensional structure of propan-2-ol is shown as A and its mirror image is shown as B. To check the superimposability of B over A, rotate B through 180° in such a way that the $\text{C}-\text{H}$ bond in the new structure C projects in the same direction as that in the structure A. Now check structures A and C. We find that A and C are superimposable. Hence propan-2-ol is an achiral molecule.

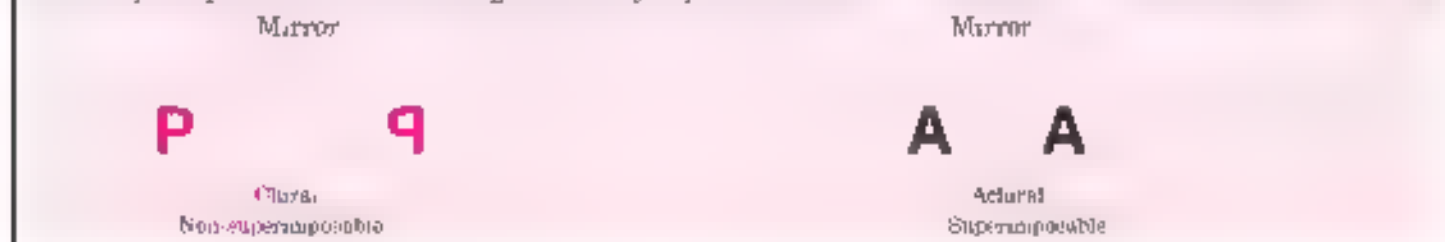


Now consider butan-2-ol. It contains one asymmetric carbon atom and therefore, it is expected to be a **chiral molecule**. Let us confirm it by superimposability test. The three dimensional structure of butan-2-ol is shown as D. Its mirror image is shown in structure E. Now rotate E through 180° in such a way that the $\text{C}-\text{H}$ bond in the new structure F projects in the same direction as that in the structure D. Now try to superimpose F over D. We observe that D and F are non-superimposable. Fig. 6 no matter how we turn or twist the molecule without breaking the bonds. As shown in Fig. 6, H_3C and H can be superimposed but the spatial orientation of H_3C and C_2H_5 are different. Therefore, butan-2-ol is a chiral molecule.



We can apply the same procedure for 2-chloropropane and 2-chlorobutane and examine them whether they are chiral or achiral. It can be easily observed that in 2-chloropropane, the mirror images are superimposable and hence it is achiral. On the other hand, the mirror images of 2-chlorobutane are non-superimposable and hence 2-chlorobutane is a chiral molecule.

The concept of chirality and achirality can also be illustrated by alphabet letters. For example, alphabet 'P' is chiral because it cannot be superimposed on its mirror image. On the other hand, alphabet 'A' is achiral because it can be superimposed on its mirror image. Similarly, alphabet letters F and J are chiral whereas M and N are achiral.



Chiral or Asymmetric Carbon

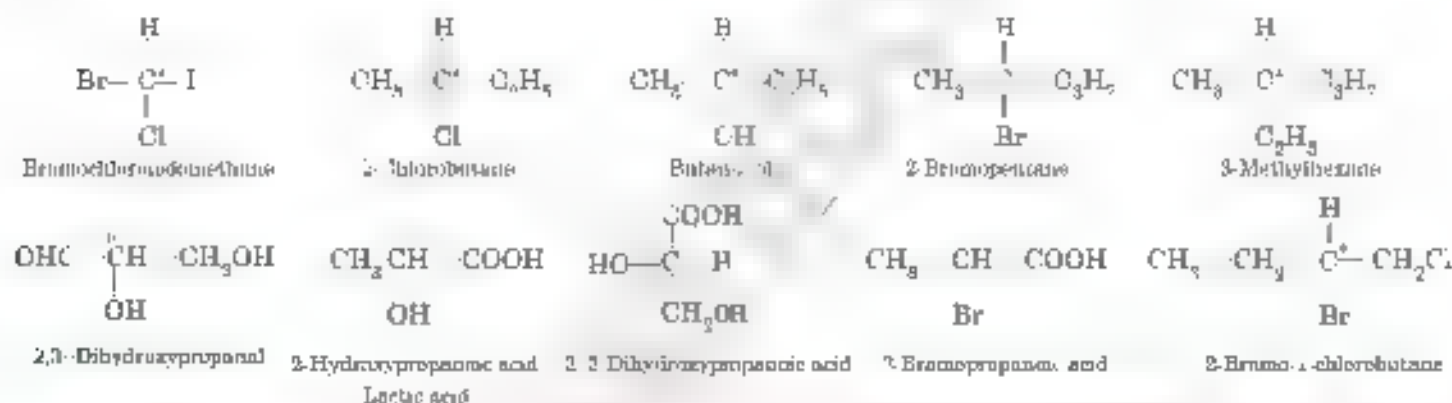
The chirality in organic compounds was studied by Van't Hoff and Le Bel. He observed that most of the organic compounds which are chiral in nature have at least one carbon atom which is bonded to four different atoms or group of atoms.

The carbon which is bonded to four different atoms or groups of atoms is called chiral or asymmetric (without symmetry) carbon atom.

It is generally indicated by asterisk as C^* . A modern term for chiral carbon is **stereogenic centre** or in short a **stereocentre**. For example, consider a hypothetical molecule C_{ABCD} where A, B, C and D are the four different substituents covalently bonded to carbon. If we place this molecule before a mirror, it is observed that it is not superimposable on its mirror image. These two non-superimposable mirror images represent two isomers or called enantiomers of the compound.

A simple example of a molecule having asymmetric or chiral carbon is bromochlorofluoromethane. It has non-superimposable mirror images.

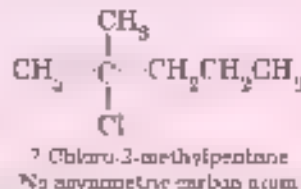
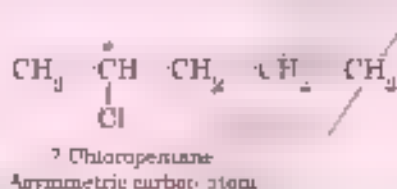
Some other examples of molecules having asymmetric or chiral carbon are



It may be noted that when a molecule contains one asymmetric carbon, it is always chiral. However, the necessary condition for chirality is not just the presence of asymmetric carbon atoms but the asymmetry of a molecule as a whole.

NOTE

The recognition of chiral or asymmetric carbon atom is very easy. We are to only see if there is any carbon atom which is bonded to four different atoms or groups in the molecule or not. For example, 2-chloropentane has asymmetric or chiral carbon but 2-chloro-2-methylpentane does not have asymmetric or chiral carbon.



Dissymmetry and Plane of Symmetry

A molecule has a **plane symmetry** if an imaginary plane when passed through the molecule bisects the molecule so that half the molecule is the mirror image of the other half. In other words, if a plane (mirror plane) when passed through the molecule divides the molecule into two symmetrical halves, the molecule is said to have a plane of symmetry. It is also called a **sigma (σ) plane**.

If we carefully observe chiral objects or molecules, it can be observed that these molecules cannot be divided into two equal and identical halves. On the other hand, achiral objects or molecules can be easily divided into two equal halves. For example, cup is achiral and it can be easily divided into two equal halves (Fig. 7). In other words, there is a plane of symmetry. However, in case of a chiral object such as hand, there is no plane (real or imaginary) which can divide it into two identical halves. Similarly, as shown in Fig. 8, an ethanol molecule has a plane of symmetry. This

plane passes through the central carbon atom, the CH_3 group and the -OH group and bisects the H-C-H bond angle. On the other hand, chiral molecules such as butan-2-ol does not have any plane of symmetry. The plane passing through the central carbon atom, CH_3 group and -OH group and bisecting the H-C-C bond angle does not divide the molecule into two identical halves. Thus, *chiral molecules do not have any plane of symmetry and therefore, are called dissymmetric. On the other hand, achiral molecules have plane of symmetry and are called symmetric.*

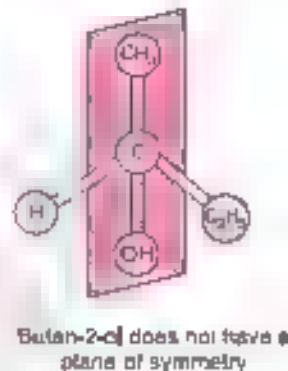
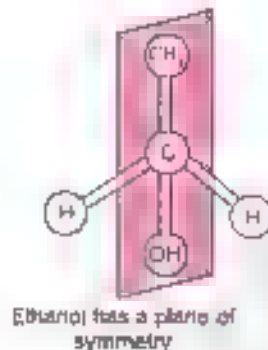
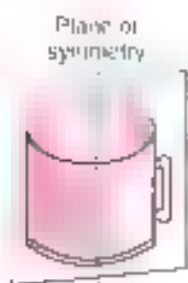


Fig. 7 Presence and absence of plane of symmetry

Fig. 8. Plane of symmetry

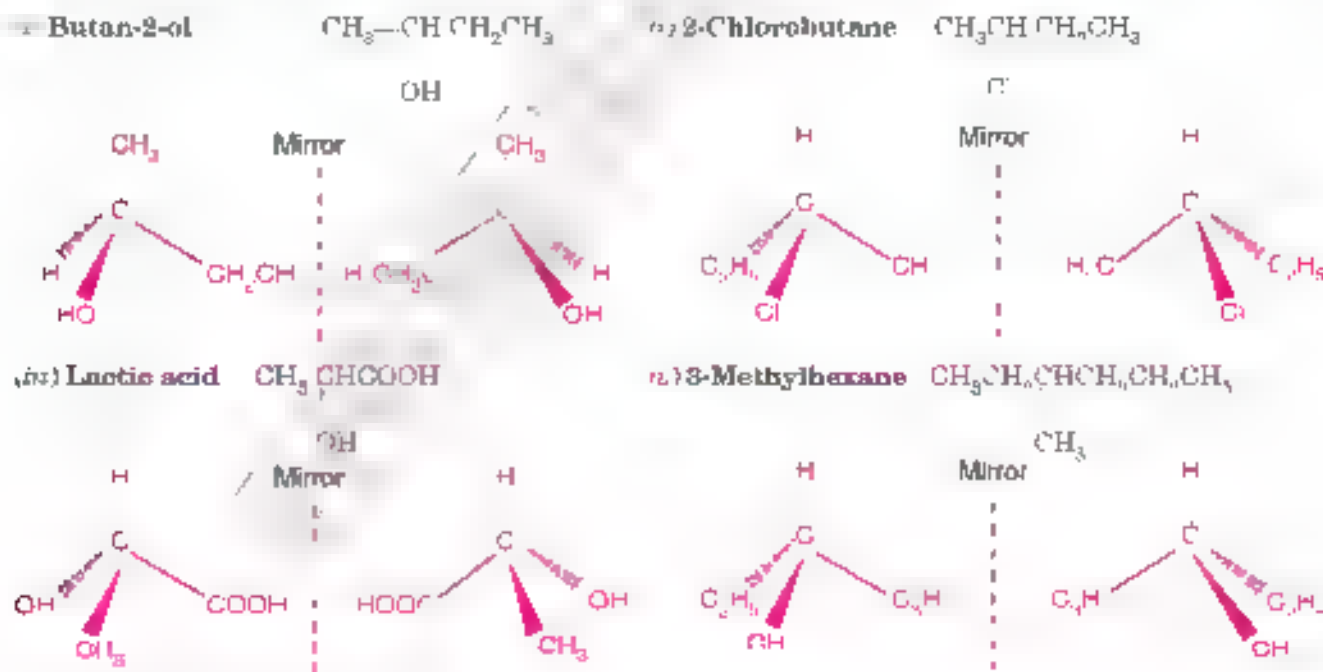
Enantiomers

The fact that butan-2-ol molecule and its mirror image cannot be superimposed shows that these are two different molecules.

These non superimposable mirror images are called **enantiomers**.

Thus, the two butan-2-ol molecules are enantiomers. It may be noted that **enantiomers must not only be mirror images, but they must also be non-superimposable**.

Similarly 2-chlorobutane, laevo and dextro leucine, etc. form non-superimposable mirror images and exist as enantiomers.



Racemic mixtures and racemisation

An equimolar mixture of the enantiomers, *dextro* and *laevo* forms, is called **racemic mixture**. It may be represented as d , or \pm forms and will be optically inactive. The process of converting d , or l form of an optically active compound into racemic form, d , is called **racemisation**. For example, on mixing equal amounts of $+$ and $-$ 2-chlorobutane, we get \pm 2-chlorobutane racemic mixture. It will have zero optical rotation because the rotation due to one isomer will be cancelled by the rotation due to the other.

Resolution

The process of separation of a racemic mixture into d- or l-forms enantiomers is called **resolution**. However whenever an optically active compound is synthesised in the laboratory, the product formed in most of the cases is a racemic mixture and thus, optically inactive. This is due to the fact that there are equal chances of the formation of the d- and l-forms. In the laboratory the physical separation of a racemic mixture i.e. resolution is not easy. Since the pair of enantiomers exhibit the same chemical and physical properties, they cannot be separated by ordinary physical or chemical methods. One of the most common methods is to allow a racemic mixture to react with an enantiomer of some other compound. This changes a racemic form into a mixture of diastereomers which have different melting and boiling points and solubilities. Then these can be separated from one another by usual methods of separation of compounds. The separated diastereoisomer is then broken down to give pure enantiomers.

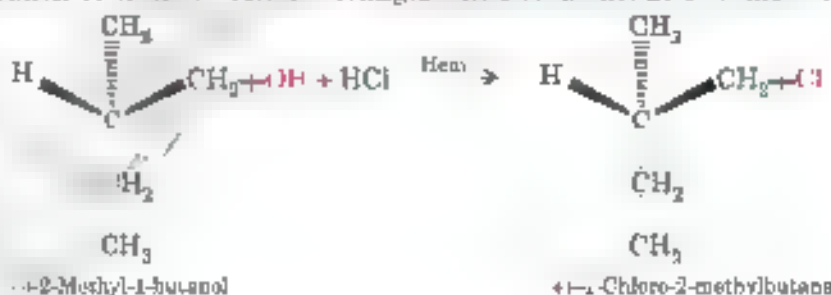
Retention

Whenever a chemical reaction is carried out on a chiral molecule the product may have the same configuration as the reactant or may have the opposite configuration. If the relative spatial arrangement of bonds at an asymmetric centre in a chiral molecule remains the same before and after the reaction, the reaction is said to occur with **retention of configuration**. In other words, retention of configuration means the preservation of integrity of the spatial arrangement of bonds at an asymmetric centre during a chemical reaction or transformation. For example, consider the following general reaction:



In this reaction there is retention of configuration because the relative configurations of the atoms b, a and c is same (i.e. clockwise from b to c) both in the reactant

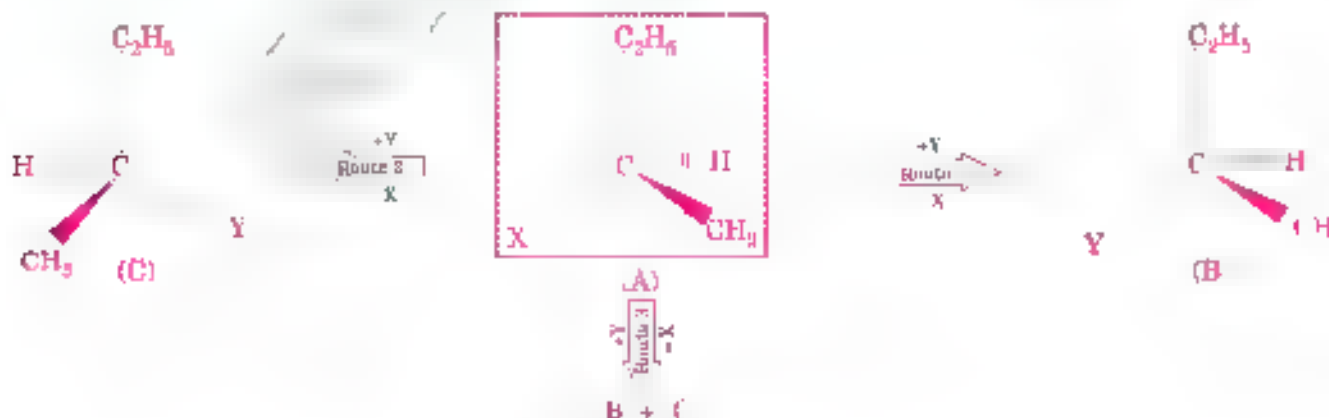
as well as in the product. In general, *during a reaction no bond to the stereocentre is broken the product will have the same general configuration of the groups around the stereocentre as that of the reactant*. Such a reaction is said to proceed with **retention of configuration**. For example, when (+)-2-methyl-butanol-1-ol is heated with concentrated HCl, (+)-1-chloro-2-methylbutane is formed.



During the reaction, no bond at the asymmetric centre is broken; therefore, the reaction proceeds with retention of configuration even though the sign of optical rotation has changed from: $[\alpha]_D^{25} +$

Outcomes of a Reaction: Inversion, retention and racemisation

When a chemical reaction involves bond cleavage or bond formation at an asymmetric carbon atom, three different products may be formed. For example, using the substitution of a group, X by Y in the following reaction, the three possible products may be shown below:



Competition Plus

Stereocenters are named according to two systems: D- and L- system and R- and S- system. For details, refer *Competition File* (page 118).

If B is the only product, the process is called **retention of configuration** because B has the same configuration as the starting reactant A.

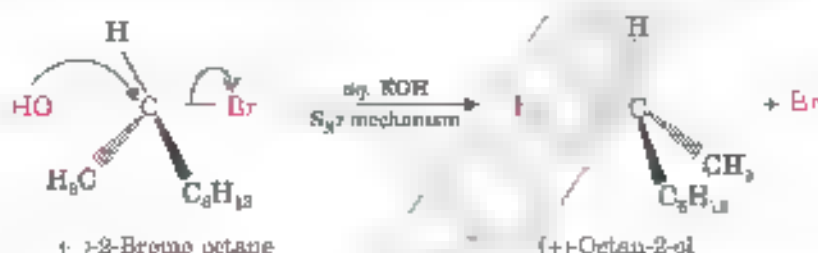
If C is the only product, the process is called **inversion of configuration** because C has the configuration opposite to the starting reactant A.

If an equimolar mixture of B and C i.e. a 50 : 50 mixture is formed, then the process is called **racemisation** and the product is **optically inactive** because one isomer will rotate light in the direction opposite to another.

Stereochemical Aspects of Nucleophilic Substitution Reactions

(a) Stereochemical aspects of S_N2 reaction

As we have learnt in S_N2 mechanism, the attack of nucleophile, OH^- occurs at the rear side of the molecule relative to the halogen atom. In other words, OH^- group has not taken the position previously occupied by the halogen atom but on the side opposite to one where the halogen atom is present. As a result, S_N2 reactions are always accompanied by inversion of configuration in much the same way as an umbrella is turned inside out in a strong wind. This process is called **inversion of configuration** or **Walden inversion**. Thus, in case of optically active alkyl halide, the product obtained has an inversion of configuration i.e. there is change in sign of rotation from $+$ to $-$ and vice versa. For example, (+)-2-bromooctane on treatment with aqueous KOH solution gives $-$ -octan-2-ol as the product.



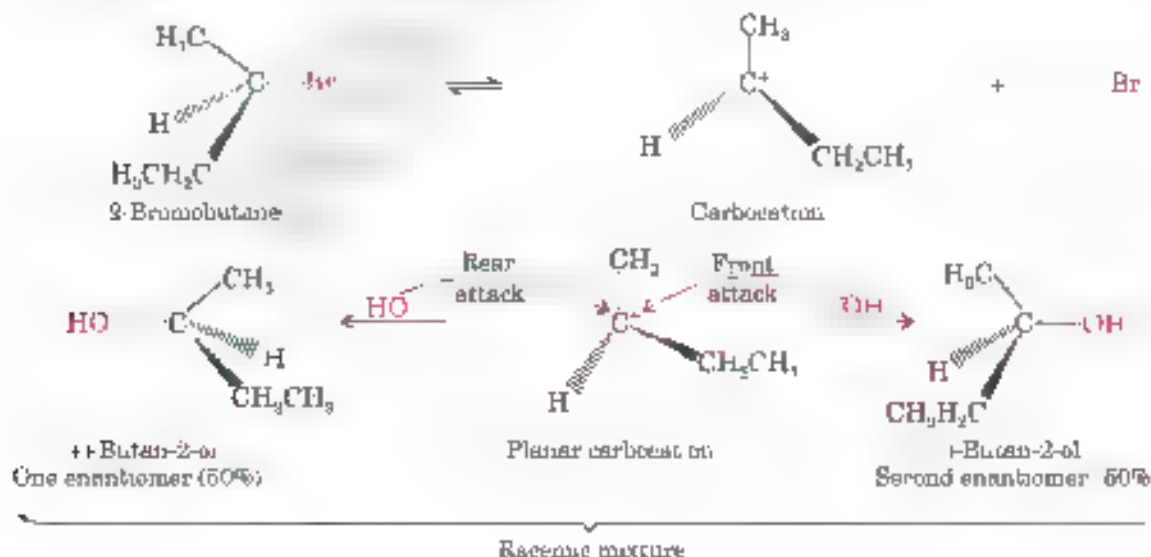
Thus, S_N2 reactions of optically active alkyl halides are accompanied by inversion of configuration.

(b) Stereochemical aspects of S_N1 reaction

In case of optically active alkyl halide, the product obtained during S_N1 reaction is a racemic mixture. This is because the intermediate carbocation formed in the slow step is planar (achiral) species. Therefore, the attack of the nucleophile, OH^- ion can take place with equal ease from both the faces (front and rear) forming a mixture of two enantiomers. In one enantiomer, the nucleophile occupies the same position as originally occupied by the halogen atom while in the other enantiomer the nucleophile occupies the position opposite to that of the halogen atom. As a result, 50 : 50 mixture of the two enantiomers, *laevo* and *dextro*, is formed. Therefore, the product formed is a racemic mixture (\pm) which is optically inactive.

Thus, S_N1 reactions of optically active alkyl halides are accompanied by racemisation.

For example, hydrolysis of optically active 2-bromobutane results in the formation of racemic mixture (\pm)-butan-2-ol.



SUM UP

S_N2 Reaction

- Nucleophile attacks from back side of X
- Bimolecular reaction involving both nucleophile and alkyl halide
- Second order reaction, rate = $k[\text{RX}][\text{Nu}^-]$
- Reactivity : $\text{CH}_3\text{X} > 1^\circ > 2^\circ > 3^\circ$
- Stereochemistry : inversion of configuration

S_N1 Reaction

- Forms carbocation which is attacked by nucleophile
- Unimolecular reaction involving only R_3CX molecule
- First order reaction, rate = $k[\text{RX}]$
- Reactivity : $3^\circ > 2^\circ > 1^\circ$
- Stereochemistry : Racemisation

For a given alkyl group, the reactivity of the halide, $\text{R}-\text{X}$ follows the same order in both the mechanisms : $\text{R}-\text{I} > \text{R}-\text{Br} > \text{R}-\text{Cl} > \text{R}-\text{F}$

Effect of solvent

S_N2 : Protic solvents decrease the rate of S_N2 reaction but polar aprotic solvents increase the rate of S_N2 reaction

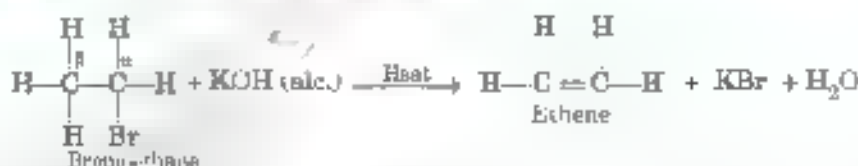
S_N1 : Polar solvents increase the rate of S_N1 reaction because these stabilize the intermediate carbocation.

Protic and Aprotic Solvents

- The solvents from which protons H^+ ions can be derived are called **protic** or **protonic solvents**. Therefore, these solvents contain ionisable hydrogen H^+ . Common examples are water H_2O , acids H_2SO_4 , alcohols, etc.
- The solvents from which protons H^+ ions cannot be ordinarily derived are called **aprotic** or **non-protonic solvents**. Therefore, these solvents do not contain ionisable hydrogen H^+ . Common examples are benzene C_6H_6 , carbon tetrachloride CCl_4 , chloroform CHCl_3 , acetonitrile CH_3CN , dimethyl formamide (DMF), dimethyl sulphoxide (DMSO), acetone CH_3COCH_3 , etc.

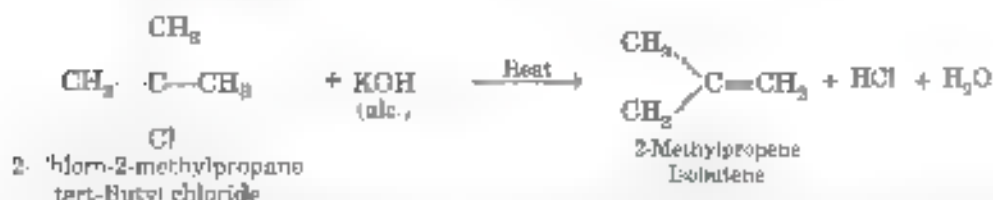
B. Elimination Reactions (Dehydrohalogenation)

When alkane with β -hydrogen atom is heated with concentrated solution of potassium hydroxide, they undergo elimination of hydrogen halide HX resulting in the formation of alkenes.

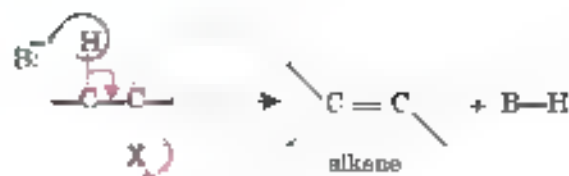


These reactions are called **β -elimination reactions** because the hydrogen atom present at β -position of the alkane or at the carbon atom next to that which carries the halogen is removed.

Similarly 1-chlorobutane on elimination gives but-1-ene and 2-chloro-2-methylpropane on elimination gives 2-methylpropene

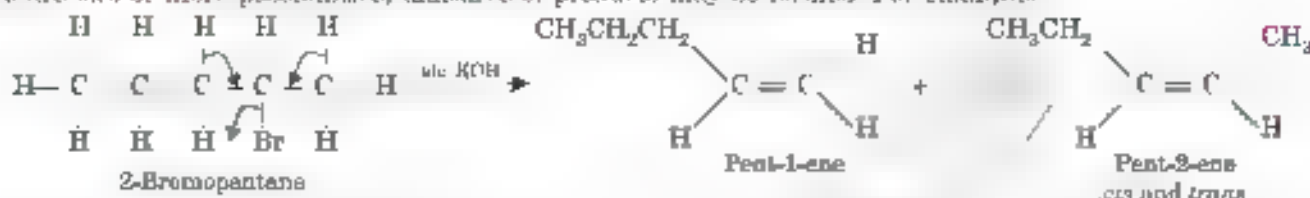


Such reactions are also called **dehydrohalogenation** removal of hydrogen halide reactions. The elimination reaction occurs by abstraction of proton from a carbon atom next to the carbon bearing halogen atom called β -hydrogen, and a halide ion is also lost resulting a new π -bond as

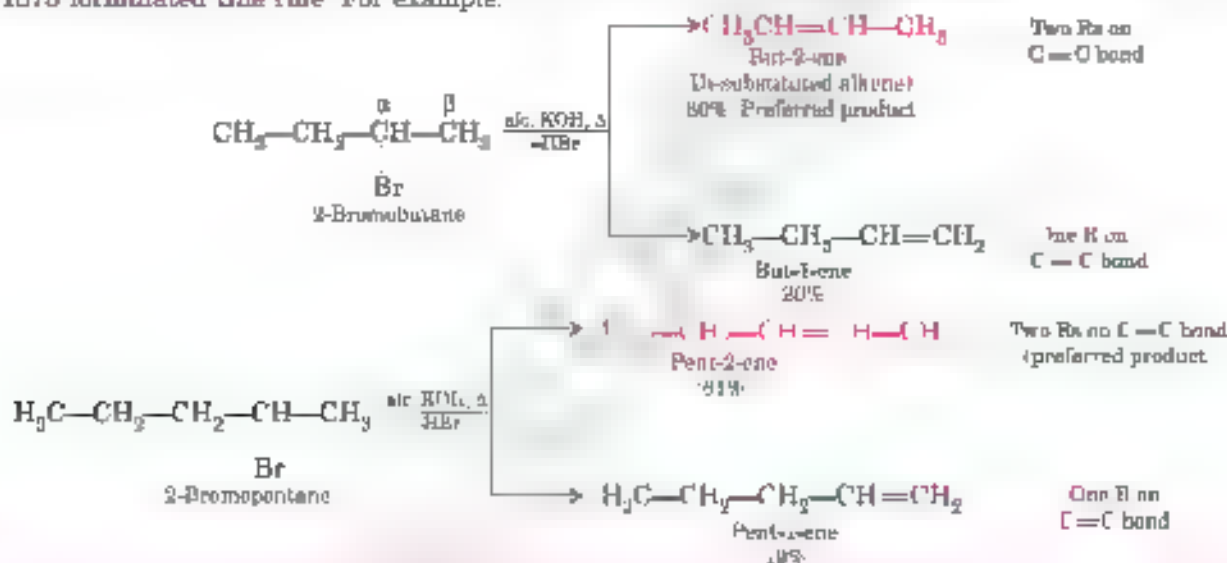


(where **B** = Base and **X** = Leaving group)

If there are two or more possibilities, mixtures of products may be formed. For example,

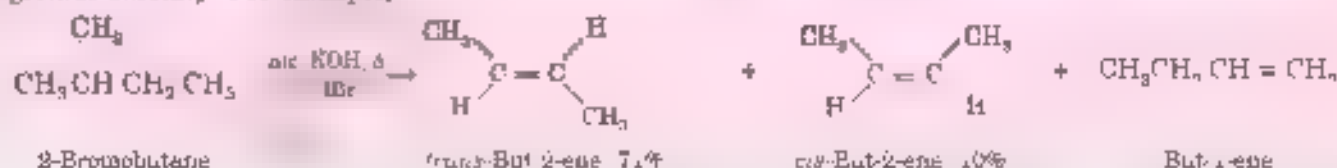


Many compounds can eliminate in more than one way to give a mixture of products. **In case a haloalkane can eliminate hydrogen halide in two different ways, then that alkene will be preferred in which carbon atoms joined by the double bond are maximum alkylated i.e. carry a larger number of alkyl groups.** This rule is called **Saytzeff's rule** after the name of Russian chemist Alexander Saytzeff (also pronounced as Saytzeff) who in 1875 formulated this rule. For example,



NOTE

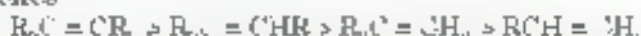
Cis-trans isomerism of Saytzeff products. If the substituted alkene formed during elimination is capable of showing *cis-trans* isomerism, then *trans*-alkene is always preferably formed as the major product because of its greater stability. For example,



Ease of dehydrohalogenation

According to Saytzeff's rule, the alkene with greater number of alkyl groups is more easily formed, i.e. the preferred product during dehydrohalogenation of alkyl halide because it is formed faster than the other alkene.

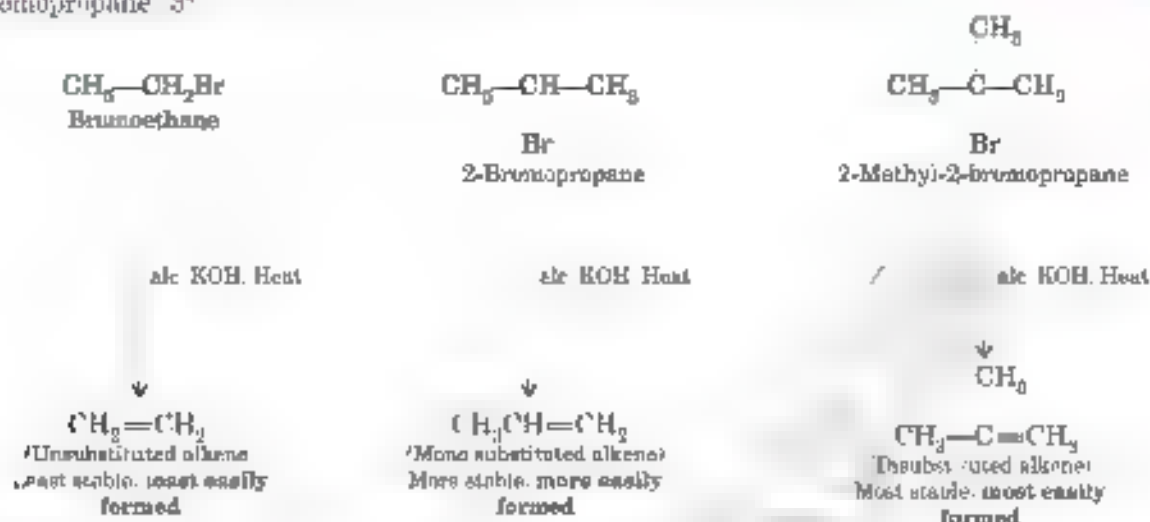
Ease of formation of alkenes



The stability of alkenes follows the same sequence. Thus, we can say that **the more stable the alkene, the faster it is formed**.

In the light of Saytzeff's rule, any alkyl halide which gives a more stable i.e. more highly substituted alkene must undergo dehydrohalogenation reaction faster than the one which gives a less stable i.e. less highly

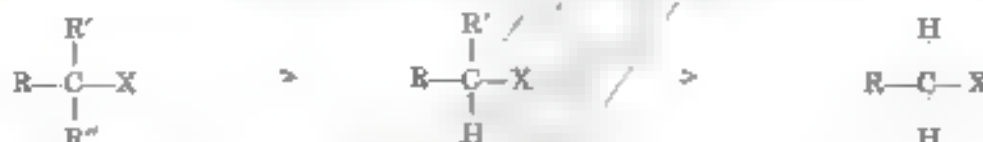
substituted alkene. For example, consider the dehydrohalogenation of bromoethane (1°), 2-bromopropane (2°) and 2-methyl-2-bromopropane (3°).



Thus, the ease of dehydrohalogenation of these three alkyl halides follows the order
2-Methyl-2-bromopropane > 2-Bromopropane > Bromoethane

In general,

The reactivity of haloalkanes towards elimination reaction, i.e. ease of dehydrohalogenation follows the order
tertiary (3°) > secondary (2°) > primary (1°)



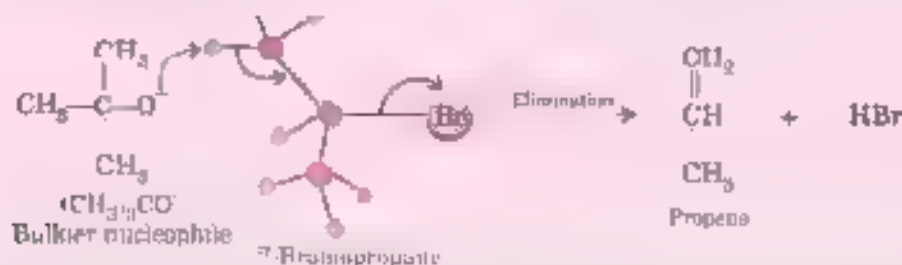
For a given alkyl group, the order of reactivity is

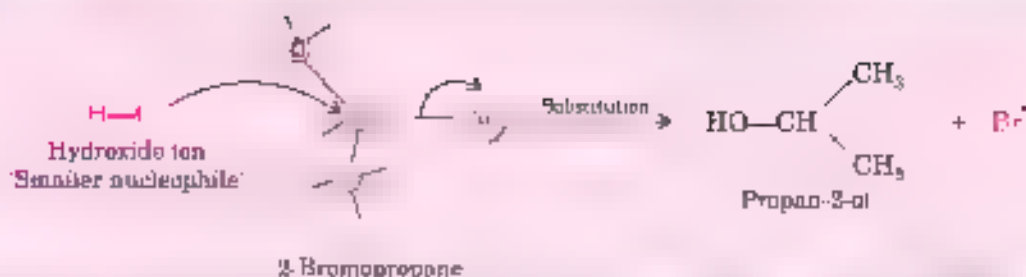


It may be noted that alcoholic KOH causes **elimination** in the molecule of haloalkane while an aqueous solution of the base leads to **substitution**. In aqueous medium the base ionises to give OH^- ions which can act as nucleophile and bring about the nucleophilic substitution. In aqueous medium, these ions also take up water molecules and get hydrated. The hydrated ion is not in a position to abstract a proton from the β -carbon atom and therefore, the elimination does not occur.

Elimination versus Substitution

We have seen that alkyl halides undergo substitution and elimination reactions. When another atom replaces the halide ion, the reaction is a **substitution** whereas when halide ion leaves with another atom or ion (often H^+) the reaction is **elimination**. Since substitution and elimination reactions often compete with each other. Most bases are also nucleophiles and therefore, they engage in substitution or elimination depending upon the alkyl halide and the reaction conditions. An alkyl halide with β -hydrogen atom when reacted with a base or a nucleophile has two competing routes, that is, $\text{S}_{\text{N}}1$ or $\text{S}_{\text{N}}2$ and elimination. Which route will be followed depends upon the nature of alkyl halide, strength and size of base or nucleophile and reaction conditions. For example, a bulkier nucleophile will prefer to act as a base and abstract a proton rather than approach a tetrahedral carbon because of steric hindrance and vice versa. For example, when 2-bromopropane is treated with a bulkier nucleophile such as potassium tert-butoxide, elimination occurs to form an alkene. On the other hand, when it is treated with a smaller nucleophile such as OH^- ion, substitution occurs to form an alcohol as shown below.





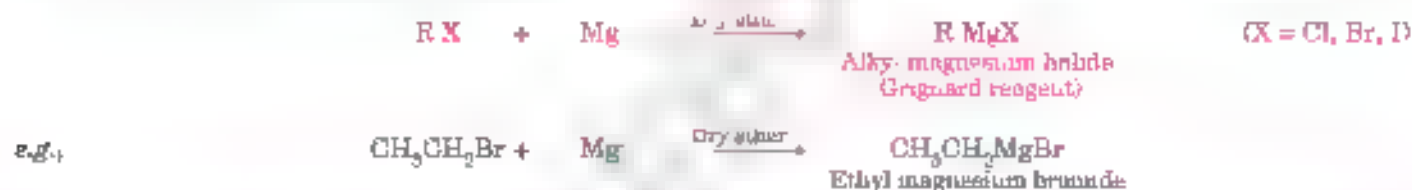
Similarly, a primary alkyl halide will prefer S_N2 reaction because primary carbocation are not very stable. On the other hand, a secondary alkyl halide can undergo S_N2 or elimination reaction depending upon the strength of base or nucleophile while a tertiary alkyl halide may undergo S_N1 or elimination, depending upon the stability of carbocation or the more substituted alkene.

In general, elimination reactions require higher temperatures than substitution reactions. This is because a larger number of bonds are broken in elimination reactions as compared to substitution reactions in which only one bond is broken. As a result, the activation energy of elimination reactions is greater than that of substitution reactions.

C. Reactions with Active Metals

Active metals like sodium, magnesium, cadmium, lithium, etc., readily combine with alkyl chlorides, bromides and iodides to give compounds containing carbon-metal bonds. Such compounds are called **organometallic compounds**.

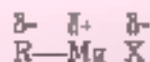
(i) Action with magnesium (formation of Grignard reagent) When a solution of an alkyl halide in dry ether is treated with magnesium, an **alkyl magnesium halide** is formed.



Alkyl magnesium halides, generally represented as $RMgX$, are important class of organometallic compounds and are known as **Grignard reagents**. These were discovered by Victor Grignard, a French chemist in 1900 and are named after his name. For this discovery Grignard got the Nobel Prize in chemistry in 1912. These compounds have great synthetic applications and are useful in the preparation of a large number of organic compounds.

Vinyl and aryl halides also form Grignard reagents.

In the Grignard reagent, the carbon-magnesium bond is covalent but highly polar with carbon pulling electrons from electropositive magnesium. This is because of large electronegativity difference between carbon (2.5) or lithium (1.2). The δ^- on carbon-halogen bond is essentially ionic. Thus Grignard reagents may be represented as



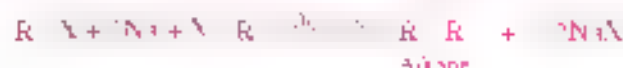
These Grignard reagents are very reactive compounds. They react with any source of proton to form hydrocarbon. Even weakly acidic compounds such as water, alcohol, amines, terminal alkynes etc. react with Grignard reagent to give corresponding hydrocarbon.

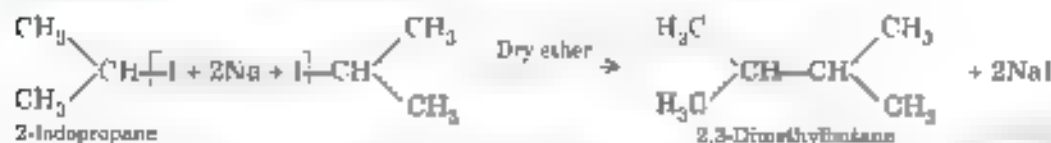


where Z may be OH, RO, NH, RNH, R₂N etc.

Therefore, it is very necessary to avoid even traces of moisture from a Grignard reagent during its preparation. These also react readily with oxygen and carbon dioxide. Therefore, these should be prepared and used in the absence of air under inert atmosphere.

(ii) Action with sodium. Two molecules of alkyl halides (same or different) react with metallic sodium in the presence of ether to form alkanes. This reaction is called **Wurtz reaction** and is used to prepare symmetrical alkanes.





This reaction generally fails with tertiary alkyl halides because under the basic conditions of the reaction they prefer to undergo dehydrohalogenation to form alkenes.

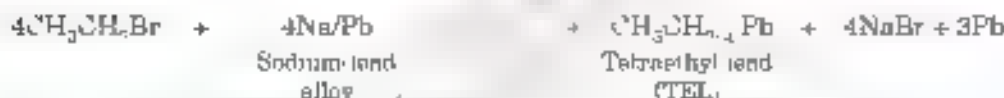
When a mixture of two different alkyl halides are used, all the three possible alkanes are formed



For example,



(iii) **Reaction with other active metals (formation of organometallic compounds).** In addition to magnesium and sodium, alkanes also react with other active metals such as lithium, zinc, mercury, etc. in the presence of dry ether to form the corresponding **organometallic compounds**. For example,



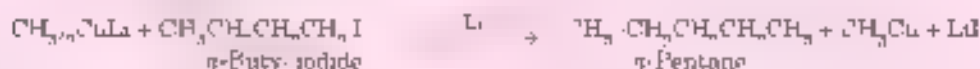
Tetraethyl lead (TEL) is used as an **anti knocking agent** in gasoline used for running automobiles.

Alkyl lithiums have chemistry similar to that of alkyl magnesium halides. One of the most valuable reactions of alkyl lithiums are their use in preparing **organocopper compounds** R_2CuLi called **Simmons reagents**. These reagents are easily prepared by the reaction of an alkyl lithium with copper(I) iodide in ether solvent. These react with alkyl chlorides, bromides and iodides forming a hydrocarbon product. In this reaction, the alkyl group of lithium reagent replaces the halogen of the alkyl halide forming a new carbon-carbon bond and yielding a hydrocarbon product.

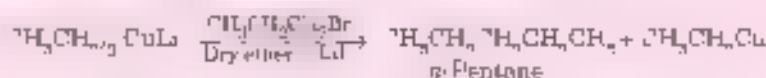
Recently Corey and House suggested a method for preparing symmetrical and unsymmetrical alkanes. This method is known as **Corey House reaction** and involves the coupling of the alkyl groups of two alkyl halides to produce an alkane.



In this method, one alkyl halide is first converted into lithium dialkyl copper and then treated with other alkyl halide. For example



Similarly

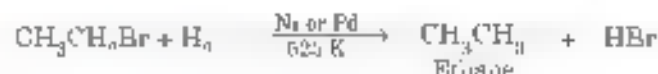


It may be noted that the alkyl halide must be either a **methyl halide** or a **primary alkyl halide**. The two alkyl groups being coupled may not be different.

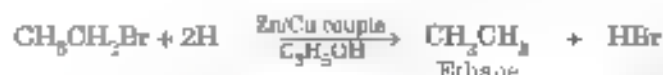
D. Reduction

Haloalkanes are reduced to corresponding alkanes by a variety of reagents

- (i) With hydrogen in the presence of a metal catalyst such as nickel, platinum or palladium



- (ii) With zinc copper couple and ethyl alcohol (95%).



- (iii) Hydroiodic acid in the presence of red phosphorus



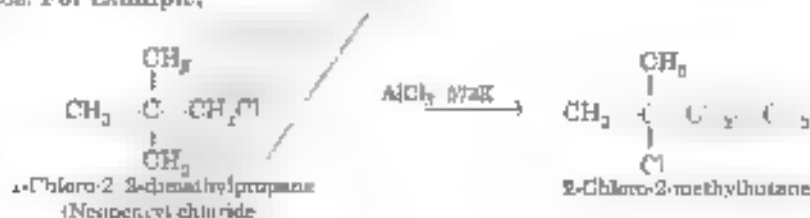
Reduction of haloalkanes can also be carried out by Zn/HCl , Sn/HCl , LiAlH_4 (lithium aluminium hydride) or NaBH_4 (sodium borohydride).

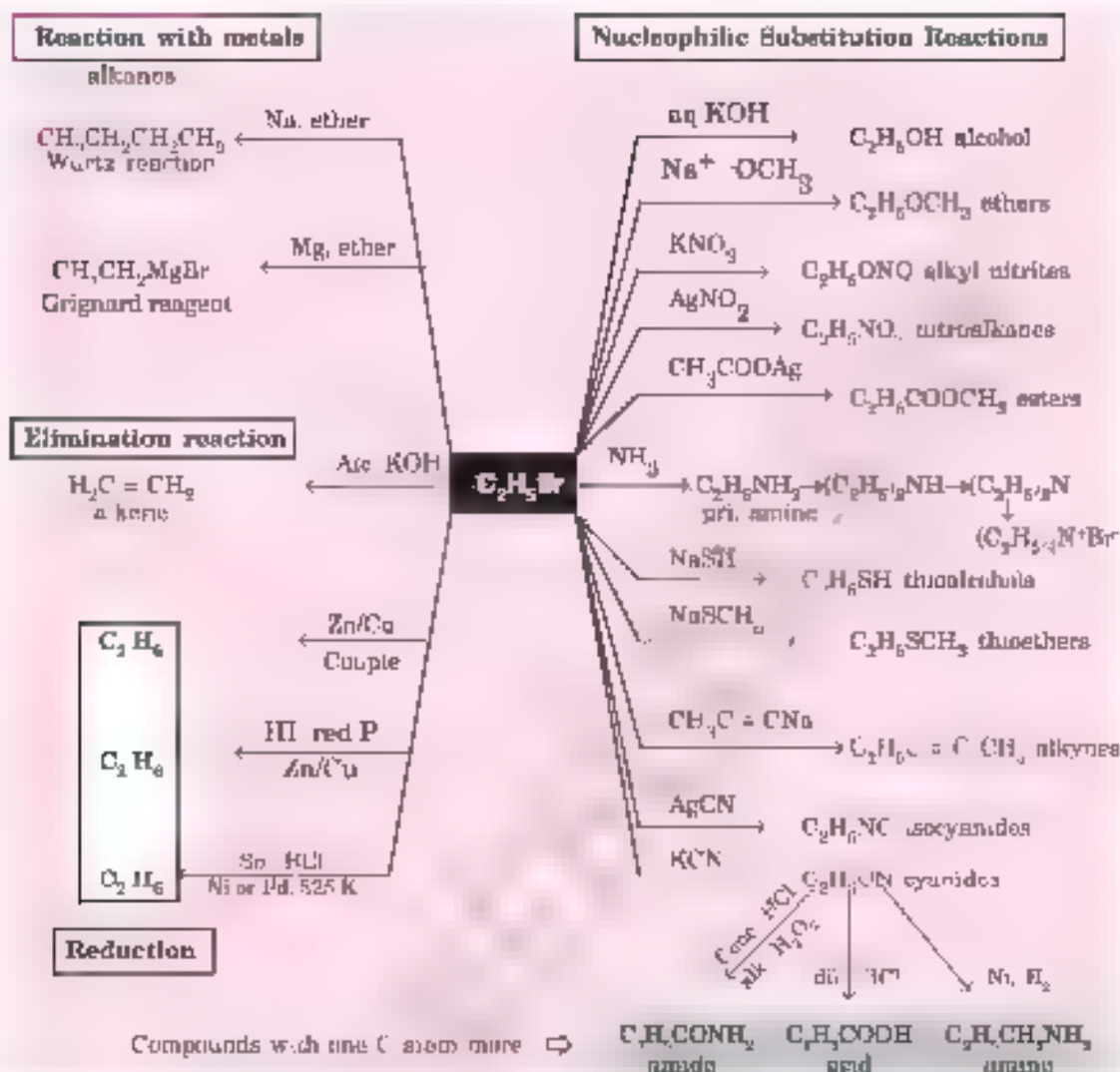
E. Rearrangement

When a haloalkane is heated at 573K or at a lower temperature in the presence of anhydrous aluminium chloride as catalyst, the haloalkane undergoes rearrangement to form a more stable alkane. This reaction is called **isomerism**.



If there is no hydrogen atom on the carbon atom adjacent to the C—X group, rearrangement occurs in which methyl group migrates. For example,

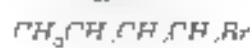
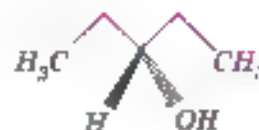
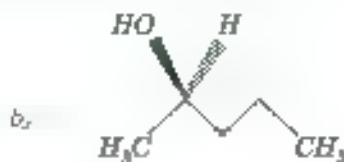
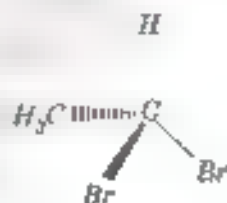
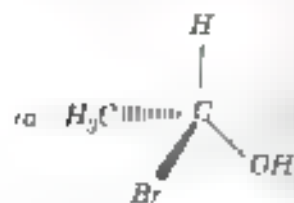




SOLVED EXAMPLES

□ Example 11

Identify chiral and achiral molecules in each of the following pairs of compounds



(N I E R T)

Solution

- a. In structure (a), the central carbon atom is bonded to four different substituents: H, OH, Br and CH_3 and hence (a) is chiral.
 Structure (b) has two identical Br atoms attached to central carbon atom and hence it is achiral molecule.
 b. (c) is chiral and (d) is achiral.
 c. (e) is chiral and (f) is achiral.

Example 12

(a) Identify the chiral molecule in the following



A.I.S.B. 2014

(b) Which alkyl halide from the following pair is chiral and undergoes faster S_N2 reaction?



(c) Out of S_N1 and S_N2 , which reaction occurs with

(i) Inversion of configuration

(D.S.B. 2014)

(ii) Racemization

(J.S.B. 2014)

(d) Identify the chiral molecule in the following pair

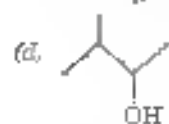


(A.I.S.B. 2018)

(e) Write the structure of alkene formed by dehydrohalogenation of 1-bromo-1-methylcyclohexane with alcoholic KOH

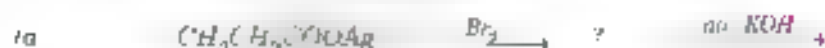
A.I.S.B. 2018

Solution

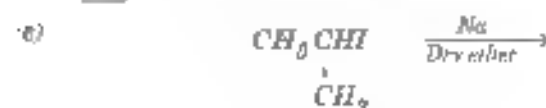


Example 13

Complete the following reactions giving major products.



(D.S.B. 2014)

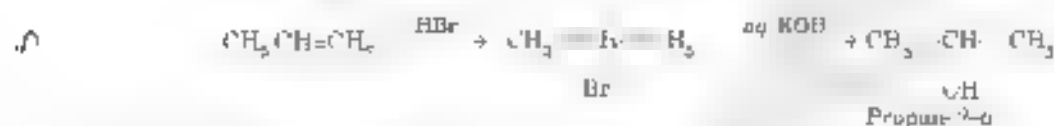
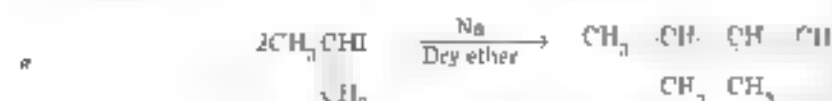
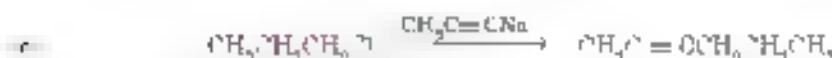




(Thurkhand S.B. 2019)



(H.P.S.B. 2015)

Solution**Example 14**

Predict the order of reactivity of the following compounds in $\text{S}_{\text{N}}1$ and $\text{S}_{\text{N}}2$ reactions

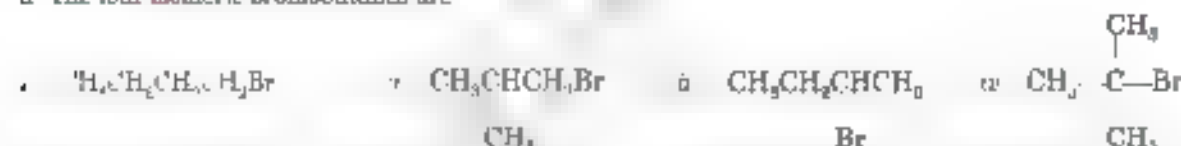
(a) The four isomeric bromobutanes



(N.C.B.R.T.)

Solution

a) The four isomeric bromobutanes are



In $\text{S}_{\text{N}}1$ reactions, the order of reactivity depends upon the stability of the intermediate carbocations. Since the stability of carbocation decreases as $3^\circ > 2^\circ > 1^\circ$, the order of reactivity also decreases in the same order. i and ii are primary alkyl bromides, but the carbocation intermediate derived from $\text{CH}_3\text{CH}_2\text{CH}(\text{Br})\text{CH}_3$ is more stable than that derived from $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{Br}$ because of greater electron donating inductive effect of $(\text{CH}_3)_2\text{CH}$ group. Therefore, $\text{CH}_3\text{CH}_2\text{CH}(\text{Br})\text{CH}_3$ is more reactive than $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{Br}$ in $\text{S}_{\text{N}}1$ reactions. iii is a secondary and iv is tertiary bromide. Hence the order of reactivity in $\text{S}_{\text{N}}1$ reaction is



The reactivity in $\text{S}_{\text{N}}2$ reactions follows the reverse order as the steric hindrance around the electrophilic carbon increases in that order. Thus, the order of reactivity in $\text{S}_{\text{N}}2$ reactions is



b) In $\text{S}_{\text{N}}1$ reactions, the reactivity increases with increase in stability of the intermediate carbocations formed as $3^\circ > 2^\circ > 1^\circ$. Therefore $\text{C}_6\text{H}_5\text{C}(\text{CH}_3)_2\text{Br}$ which gives 3° carbocation i.e. $(\text{C}_6\text{H}_5)_2\text{C}^+\text{CH}_3$ is the most reactive. Of the two secondary bromides, $\text{C}_6\text{H}_5\text{CH}(\text{C}_6\text{H}_5)\text{Br}$ and $\text{C}_6\text{H}_5\text{CH}(\text{CH}_3)\text{Br}$, the carbocation intermediate obtained from $\text{C}_6\text{H}_5\text{CH}(\text{C}_6\text{H}_5)\text{Br}$ i.e. $(\text{C}_6\text{H}_5)_2\text{CH}^+$ is more stable than that obtained from $\text{C}_6\text{H}_5\text{CH}(\text{CH}_3)\text{Br}$ i.e. $(\text{C}_6\text{H}_5)\text{CH}^+\text{CH}_3$ because it is stabilised by two phenyl groups due to resonance. Therefore, $\text{C}_6\text{H}_5\text{CH}(\text{C}_6\text{H}_5)\text{Br}$ is more reactive than $\text{C}_6\text{H}_5\text{CH}(\text{CH}_3)\text{Br}$.

The fourth alkyl bromide i.e. $\text{C}_6\text{H}_5\text{CH}_2\text{Br}$ which gives primary carbocation i.e. $\text{C}_6\text{H}_5\text{CH}_2^+$ is least reactive. Hence, the overall reactivity of these alkyl bromides towards $\text{S}_{\text{N}}1$ reactions decreases as:

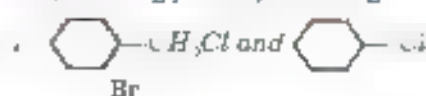


In S_N2 reactions the reactivity depends upon the steric hindrance and decreases as $3^\circ > 2^\circ > 1^\circ$. Therefore, primary bromide, $(CH_3)_3CH_2Br$ is most reactive and tertiary bromide $(CH_3)_3CBr$ is least reactive. Among two secondary bromides, $(C_6H_5)_2CHCH_2Br$ is less reactive than $(CH_3)_2CHCH_2Br$ because a phenyl group is bulkier than a methyl group and causes more steric hindrance. So, the correct order is

For S_N2 reaction $C_2H_5OC(CH_3)_3Br < C_6H_5CH(CH_3)CH_2Br < C_6H_5CH_2CH_2Br < C_6H_5CH_2Br$

Example 16.

(a) In the following pairs of the halogen compounds, which would undergo S_N2 faster?



A.C.E.R.T. A.I.S.B. 2009

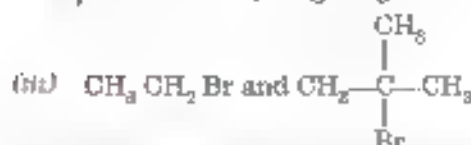


(D.S.B. 2015)

(b) Which one of the following pairs undergoes S_N1 substitution reaction faster and why?





A.I.S.B. 2009



(A.I.S.B. 2015)

Solution a. S_N2 reaction proceeds through the formation of a transition state involving bonding of carbon to five atoms or groups. The reactivity is decided by stability of transition state on the basis of steric hindrance. The reactivity follows the order $CH_3 > 1^\circ > 2^\circ > 3^\circ$ halide. Therefore,

 CH_2Cl is primary alkyl halide and hence undergoes S_N2 reaction faster

 I will undergo S_N2 reaction faster than  Cl because iodine is a better leaving group because of its large size and hence it will be released at a faster rate in the presence of incoming nucleophile.

i.  Br 1-Bromo-2,2-dimethylpropane reacts faster because it is 1° alkyl halide




ii.  Br 2-Methyl-1-bromopropane reacts faster because it has lesser steric hindrance in the transition state


iii. CH_3CH_2Br would undergo S_N2 reaction faster because of less steric hindrance

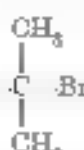
b. S_N1 reaction occurs through the formation of carbocation. Therefore, greater the stability of the carbocation, faster is the rate of S_N1 reaction. Since the stability of carbocation follows the order $3^\circ > 2^\circ > 1^\circ > (CH_3)^+$, therefore,

Out of  Cl or  Cl or  Cl reacts faster because it involves the formation of 3° -carbocation 

while  Cl involves the formation of 2° -carbocation 

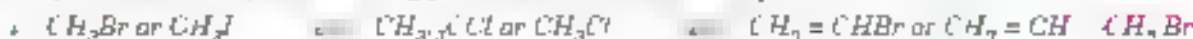
ii. Out of  Cl or  Cl or  Cl reacts faster because it forms 2° carbocation while

 Cl involves 1° carbocation.

iii.  Br undergoes S_N1 reaction faster. This is because the carbocation derived from $(CH_3)_3CBr$ is 3° carbocation and is more stable than carbocation 1° obtained from CH_3CH_2Br

Example 16.

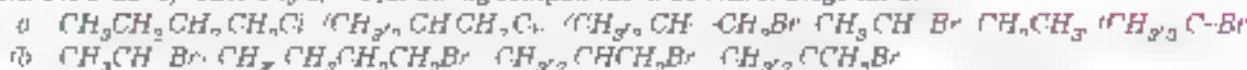
Which compound in each of the following pairs will react faster in S_N2 reaction with OH^- ?



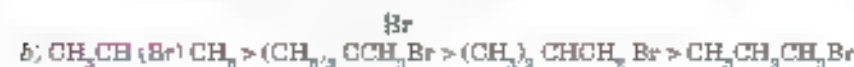
Solution. (i) CH_3I (ii) CH_3CH_2Br (iii) $CH_3CH=CHCH_2Br$

Example 17.

Predict the order of reactivity of the following compounds in dehydrohalogenation.

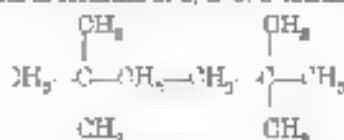


Solution. i. $CH_3CH_2CH_2CH_2CH_2Br > CH_3CH_2CH_2CH_2CH_2Cl > (CH_3)_2CHCH_2CH_2Br > (CH_3)_3CCH_2CH_2Cl > (CH_3)_3CCH_2CH_2Br$

**Example 18.**

A hydrocarbon **A** on treatment with a copper couple gives a hydrocarbon **B** with four carbon atoms. When **A** is dissolved in ether and treated with sodium, 2, 2, 5, 5-tetramethylhexane is formed. What is the formula of the compound **A**?

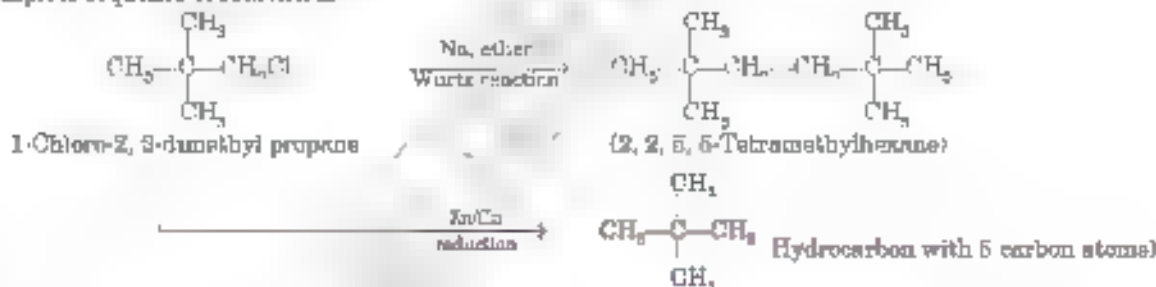
Solution. The structural formula of 2, 2, 5, 5-tetramethylhexane.



suggests that the compound **A** which gives the above compound during Wurtz reaction is



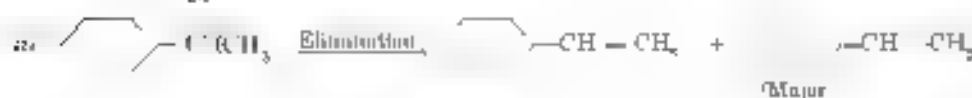
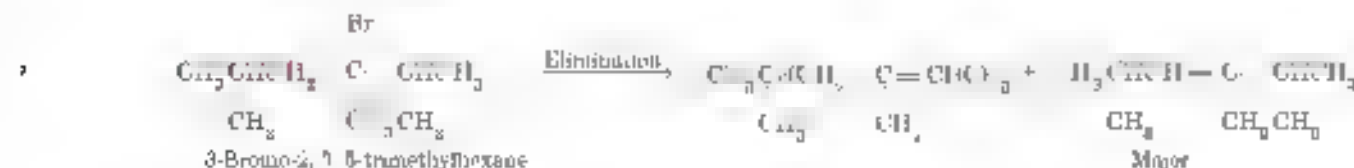
The complete sequence of reaction is

**Example 19.**

What products would you expect from the elimination of the following alkyl halides. which product will be major in each case?



Solution.



Practice Problems

10. From each of the following pairs, predict which compound will have higher boiling point
 (i) isopropyl bromide and *n*-propyl bromide (ii) bromoethane and iodoethane
 (iii) tert-butyl chloride and tert-butyl iodide (iv) iso-propyl bromide and *n*-butyl bromide
11. Arrange the following in the increasing order of boiling point
- Br
- (i) $\text{H}_3\text{C}_3\text{Br}$ (ii) $\text{H}_3\text{CCH}_2\text{CH}_2\text{Br}$ (iii) $\text{H}_3\text{CCH}_2\text{CH}_2\text{CH}_2\text{Br}$ (iv) $\text{H}_3\text{C}_4\text{Br}$
12. Which isomer of $\text{C}_4\text{H}_9\text{Cl}$ will have the lowest boiling point?
13. Which metal is used in the preparation of Grignard's reagent from haloalkanes?
14. Which of the following is most reactive alcohol for its reaction with H^+ ?
- (a) $(\text{CH}_3)_3\text{COH}$ (b) $(\text{CH}_3)_2\text{CHCH}_2\text{OH}$ (c) $\text{CH}_3\text{CH}_2\text{CH}(\text{OH})\text{CH}_3$
15. Name the reagents used to convert
 (a) 1-chloropropane to 1-nitropropane (b) Bromoethane to butane
 (c) Bromoethane to ethoxyethane (d) Bromoethane to 1-butyne (e) Bromoethane to diethyl thioether
- Give chemical reactions
16. Select the compound in each of the following pairs, that can be converted to corresponding alkyl bromide more rapidly on being treated with hydrogen bromide
- (i) 1-butanol or 2-butanol (ii) 2-methyl-1-butanol or 2-butanol
 (iii) 2-methyl-2-butanol or 2-butanol
17. Which will be the main product when the following haloalkanes are treated with alcoholic KOH ?
- 2-bromobutane (i) $\text{H}_3\text{CCH}_2\text{Cl}$ (ii) $\text{H}_3\text{C}_3\text{Cl}$
18. Predict all the alkenes that would be formed by the dehydrohalogenation of the following halides with sodium ethoxide and identify the major alkene
- (i) 2-chloro-2-methylbutane (ii) 2,2-dimethyl-3-bromopentane
 (iii) Cyclohexyl bromide (iv) 1-bromo-1-methylcyclohexane

Answers to Practice Problems

- [illegible]

CHEMICAL PROPERTIES OF HALOARENES

Haloarenes are chemically less reactive than haloalkanes. The low reactivity of haloarenes in comparison to haloalkanes is due to the following reasons:

1. **Resonance effect.** in haloarenes the electron pairs on the halogen atom are in conjugation with π -electrons of the ring and the following resonating structures are possible:



As a result of resonance, there is delocalisation of electrons on C-Cl bond which acquires a partial double bond character. This is also evident from the contribution of structures III, IV and V. As a result, the bond cleavage in

haloarenes is difficult than haloalkanes in which carbon is attached to halogen by a pure single bond. Therefore, haloarenes are less reactive towards nucleophilic substitution reactions.

2. Difference in hybridisation states of carbon atom in C—X bond. In haloalkanes, the carbon atom of the C—X bond is sp^3 hybridised while in haloarenes, the carbon atom attached to halogen is sp^2 hybridised. The sp^2 hybridised carbon atom with a greater s -character is more electronegative. It can hold the electron pair of the bond more tightly than the sp^3 hybridised carbon atom in alkyl halides with less s -character. Therefore, the C—X bond in haloarenes is shorter than in haloalkanes. This is confirmed by X-ray analysis which shows that the C—Cl bond length in chlorobenzene is 169 pm while the C—Cl bond length in ethyl chloride molecule is 177 pm. The shortening of bond length imparts stability to aryl halides and as a result, the bond cleavage becomes rather difficult. Therefore, haloarenes are less reactive than haloalkanes towards nucleophilic substitutions.



3. Polarity of carbon-halogen bond. The sp^2 hybridised carbon atom involved in C—X bond in haloarene molecule is more electronegative than the sp^3 hybrid carbon atom in alkyl halide. Therefore, this sp^2 hybridised carbon has less tendency to release electrons to the Cl atom and the C—Cl bond in aryl halides is less polar than in alkyl halides. This is supported by the fact that the dipole moment of chlorobenzene is 1.73 D while the dipole moment of chloroethane is 2.05 D. Thus, lesser the polarity of C—Cl bond, lesser is the reactivity.

4. Instability of phenyl cation. In case of haloarenes, the phenyl cation formed as a result of self ionisation will not be stabilised by resonance because the sp^2 hybridised orbital of carbon having +ve charge is perpendicular to the p -orbital of the phenyl ring. Therefore, phenyl cation is not formed and therefore S_N1 mechanism cannot occur.

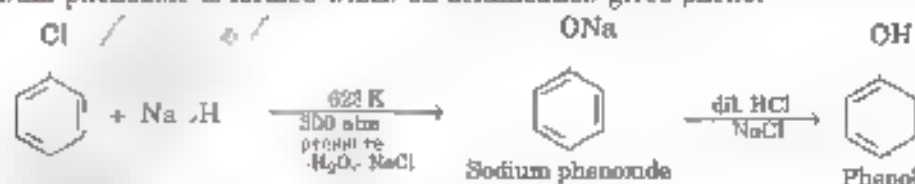


5. Repulsion between the electron rich attacking nucleophiles and electron rich arenes. Due to the electron rich arenes, electron rich nucleophile will not approach closely for the attack because of repulsion.

Thus, haloarenes are less reactive towards the substitution reactions than haloalkanes. However, under drastic conditions, aryl halides undergo substitution reactions as discussed below.

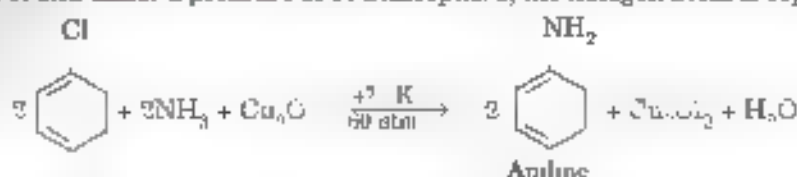
A. Nucleophilic Substitution Reactions

1. Replacement by hydroxy group (formation of phenol). On heating aryl halides with aqueous solution of sodium hydroxide at 623 K and under pressure (30 atm), the halogen atom is replaced by hydroxy group forming phenol. In the first stage sodium phenoxide is formed which on acidification gives phenol.

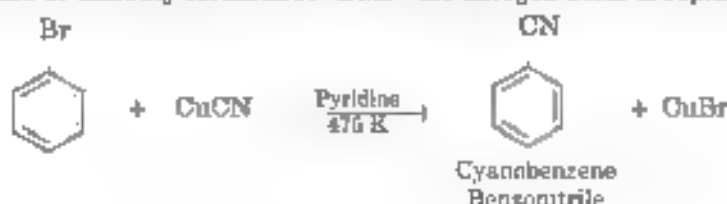


This reaction forms the basis of **Dow's process** for the manufacture of phenol.

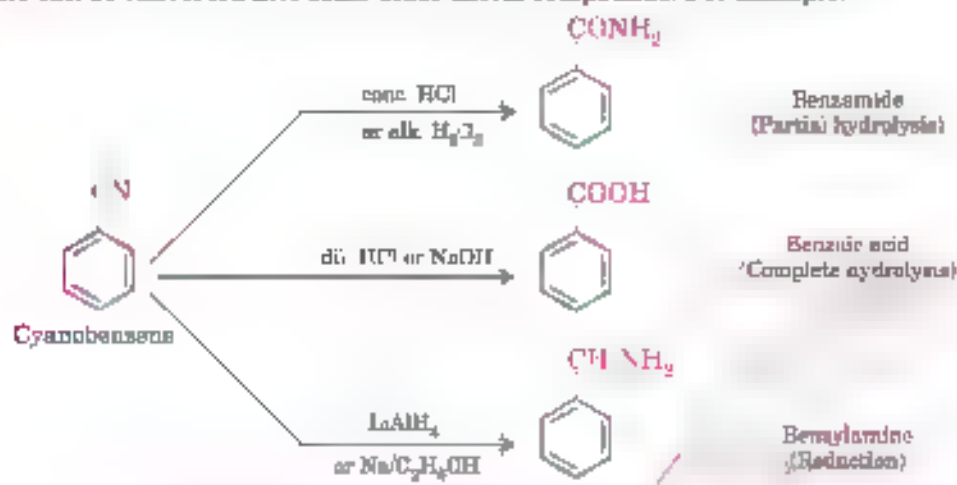
2. Substitution by amino group (formation of aniline). On heating with aqueous ammonia in the presence of cuprous oxide catalyst at 475 K and under a pressure of 80 atmosphere, the halogen atom is replaced by amino group.



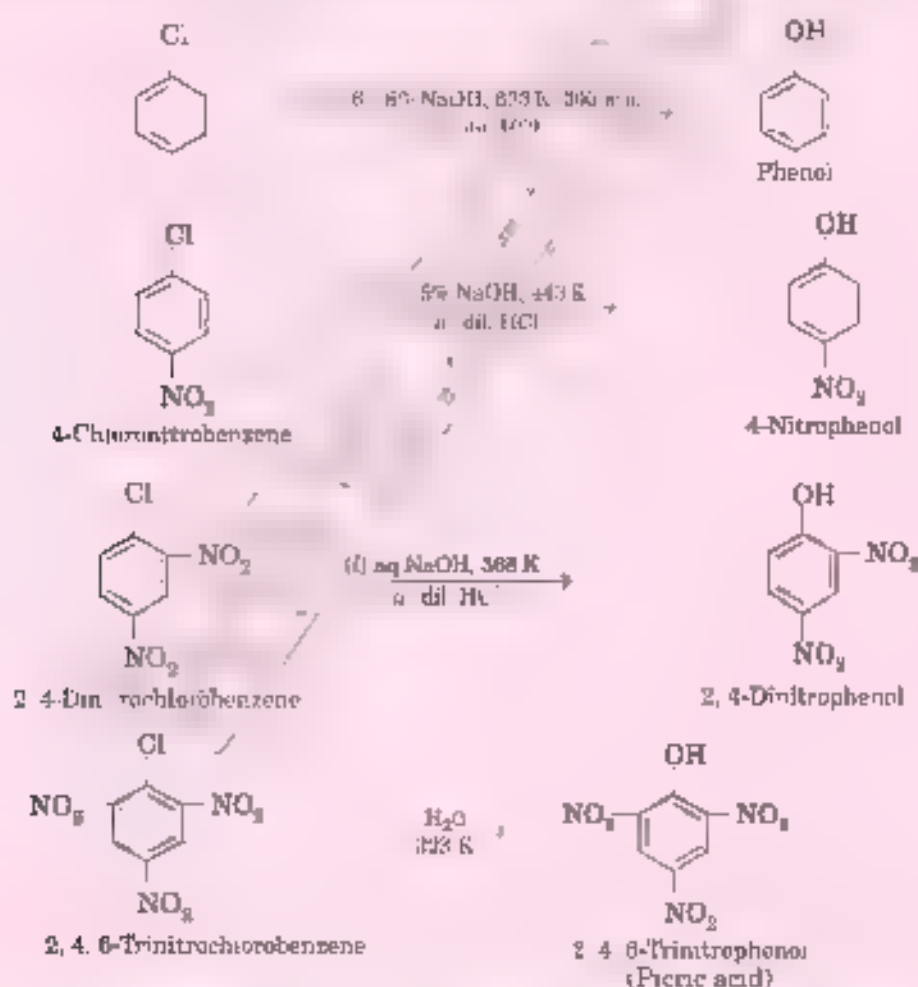
3. Substitution by cyano group (formation of cyanobenzene). On heating with anhydrous cuprous cyanide in the presence of pyridine or dimethylformamide (DMF) the halogen atom is replaced by cyano group.



The cyanobenzene can be converted into some other useful compounds. For example,



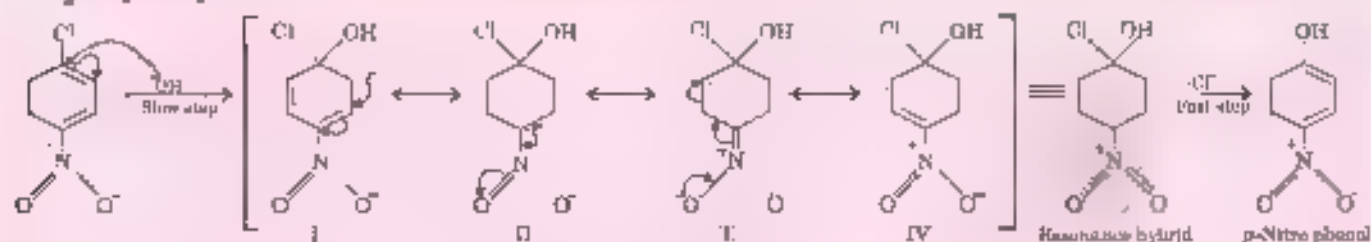
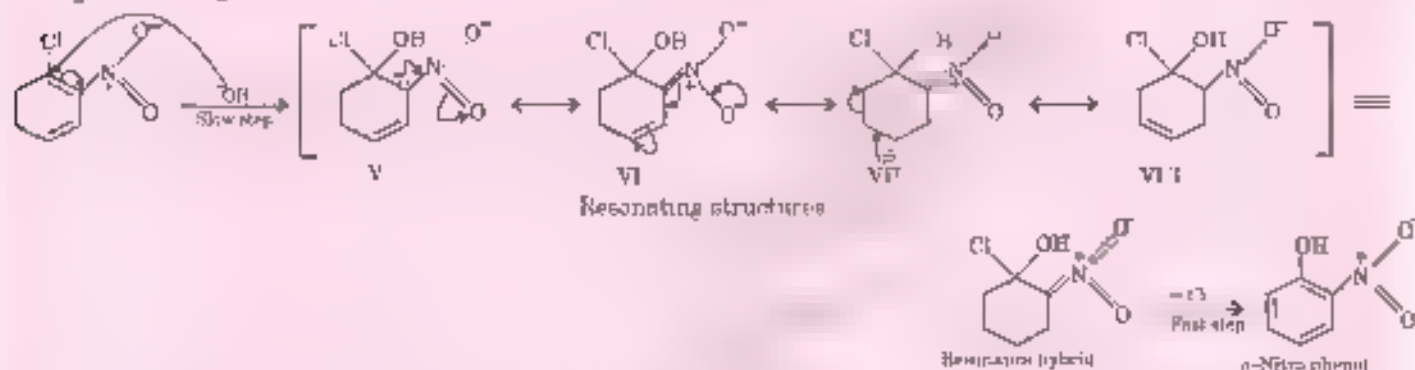
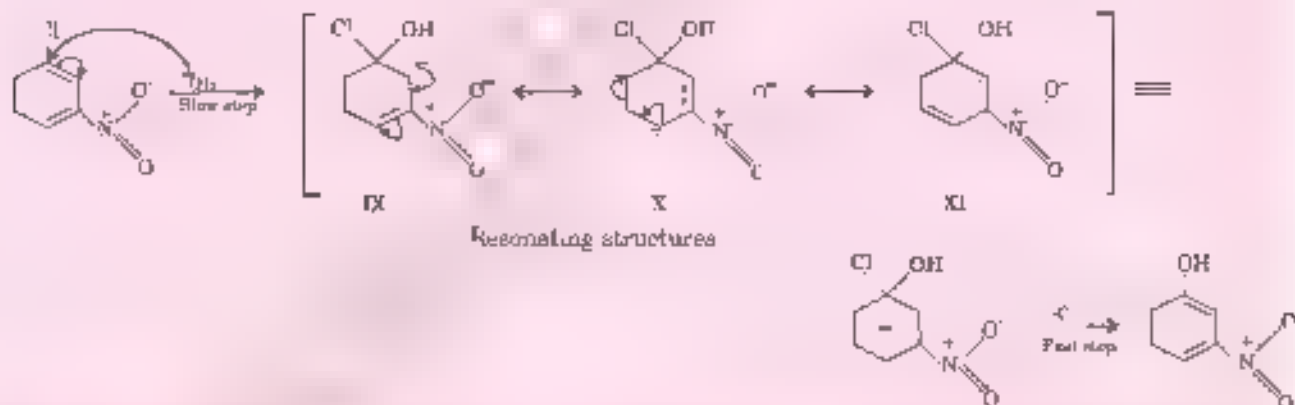
Effect of substituents in haloarenes (aryl halides) on the reactivity. The presence of certain groups at certain positions of the ring markedly affects the reactivity of haloarenes. It has been observed that the presence of **electron withdrawing groups** such as $-\text{NO}_2$, $-\text{CN}$, $-\text{COOH}$, etc. at *o*- and *p*-positions to the halogen atom greatly activates the halogen towards nucleophilic substitution reactions. For example, chlorobenzene is converted into phenol by 5-6% aqueous NaOH only at temperatures above 623 K, whereas *p*-chloronitrobenzene is converted into nitrophenol by aqueous NaOH at 473 K. As the number of ortho and para nitro groups on the ring is increased, the reactivity increases.



It may be noted that a nitro group meta to the chlorine has no effect on the reactivity.

Explanation for effect of NO_2 group

The presence of NO_2 groups at *ortho* and *para* positions withdraws electron density from the benzene ring and therefore facilitates the attack of the nucleophile on haloarenes. The carbanion that is formed is stabilized through resonance as shown below.

 NO_2 at para position **NO_2 at ortho position** **NO_2 at meta position**

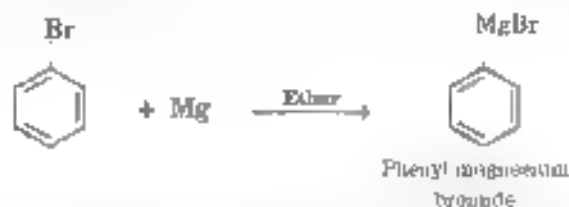
It is clear from above structures that in case of *o*- and *p*-chlorobenzenes, one of the resonating structures (II in case of *p*-nitrochlorobenzene and V in case of *o*-chlorobenzene) bears a negative charge on the carbon atom bearing the NO_2 group. Therefore, these carbanions are stabilized by the NO_2 group as well as π -electrons of the benzene ring. However, in case of *m*-nitrochlorobenzene, none of the resonating structures bear the negative charge on carbon atom bearing the NO_2 group. Therefore, the nitro group at *meta* position does not stabilize the negative charge but the carbanion is stabilized only by the π -electrons of the benzene ring. In other words, the carbanions formed from *o*-nitrochlorobenzene and *p*-nitrochlorobenzene are most stable than that formed from *m*-nitrochlorobenzene.

Thus, the presence of electron withdrawing groups at *o*- and *p*-positions (but not at *m*-positions) with halogen atom activates the aryl halides towards nucleophilic substitution reactions. Moreover, as the number of electron withdrawing groups at *o*- and *p*-position increases, the stabilization of the resulting carbanion increases due to more structures of II and V type and hence, the reactivity of the aryl halide further increases.

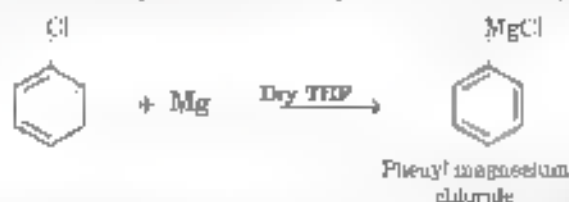
It may be noted that although the presence of NO_2 group (electron withdrawing group) at *m*-position w.r.t. the halogen does not stabilize the carbanion by resonance effect, it does stabilize it somewhat by the inductive effect as compared to the carbanion resulting from chlorobenzene itself. Therefore, *m*-nitrochlorobenzene is more reactive than chlorobenzene towards nucleophilic substitution reactions.

B. Reaction with Metals

1. **Reaction of magnesium.** Like alkyl halides, aryl bromides and iodides also react with magnesium in dry ether to form Grignard reagent



Chlorobenzene reacts with magnesium in the presence of tetrahydrofuran (THF) solvent

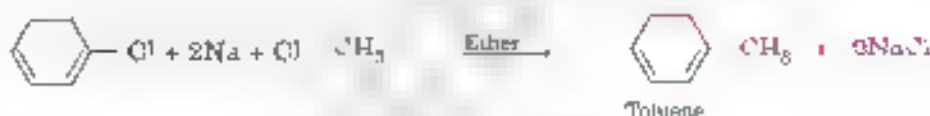


2. **Reaction with lithium.** Bromo and iodoarenes react with lithium metal in the presence of dry ether to form corresponding organometallic compounds.



3. **Reaction with sodium.**

(i) **Wurtz Fittig reaction.** When aryl halide is heated with alkyl halide in the presence of sodium in anhydrous ether, halogen atom is replaced by alkyl group. This reaction is called **Wurtz Fittig reaction**

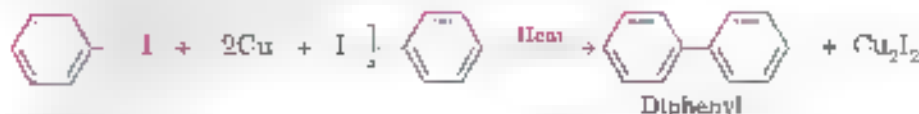


(ii) **Fittig reaction.** When haloarenes react with sodium in the presence of ether diphenyl is formed. This reaction is called **Fittig reaction**.



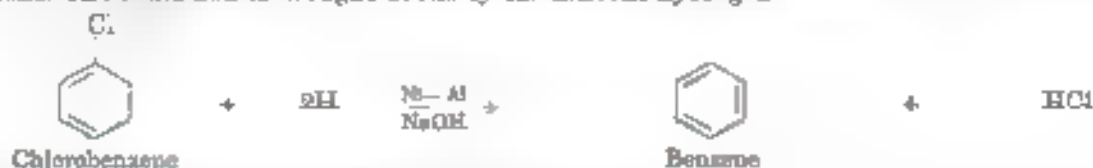
4. **Reaction with copper powder.**

Ullmann reaction. Iodobenzene when heated with copper powder in a sealed tube, it gives diphenyl. This reaction is called **Ullmann reaction** it is also called **Ullmann biaryl synthesis**.



C. Reduction

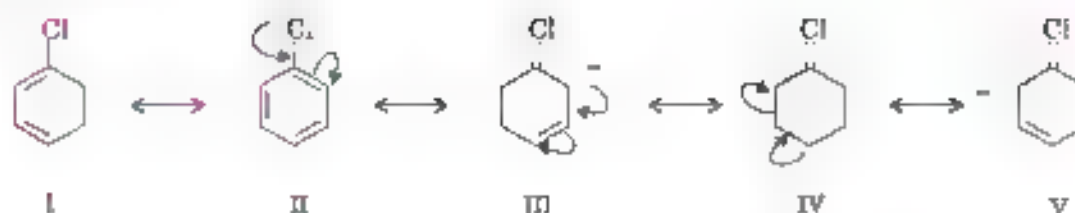
Haloarenes undergo reduction with LiAlH_4 or nickel aluminium alloy (Ni-Al) in the presence of an alkali to form hydrocarbons. The reduction is brought about by the nascent hydrogen.



D. Ring substitution or electrophilic substitution reactions

Haloarenes undergo electrophilic substitution reactions in the benzene ring. The halogen atom is ortho and para directing and therefore, substitution takes place at ortho and para positions.

The ortho and para directing effect of halogen atom can be understood if we consider the resonance structures of chlorobenzene as shown below

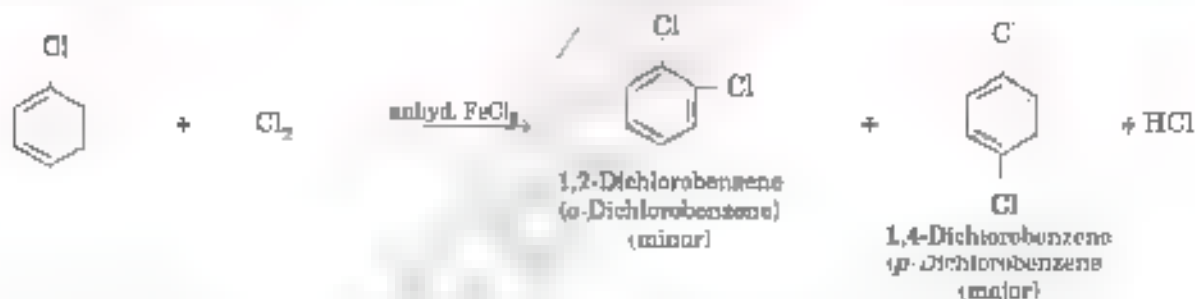


It has been seen that in structures III, IV and V the ortho and para positions get negatively charged. In other words, the electron density is relatively more at ortho and para positions and consequently the incoming electrophile is more likely to attack on these positions. However, because of steric hindrance at the ortho position, the para-product usually predominates over the ortho product. Further, it may be noted that hydrogen atom has $-I$ effect, because it is electron withdrawing group. As a result, it tends to deactivate the benzene ring. Therefore, the electrophilic substitution reactions of chlorobenzene occur slowly and under drastic conditions compared to benzene. Thus,

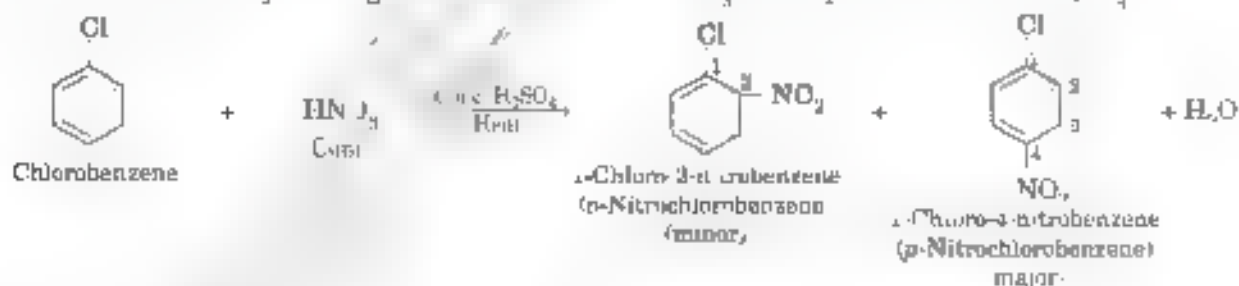
- **Remember**
- i. Haloarenes undergo electrophilic substitution reactions slowly as compared to benzene
 - ii. Halogen group is ortho and para director, para-product usually predominates over the ortho product.

Some important reactions of chlorobenzene are given below

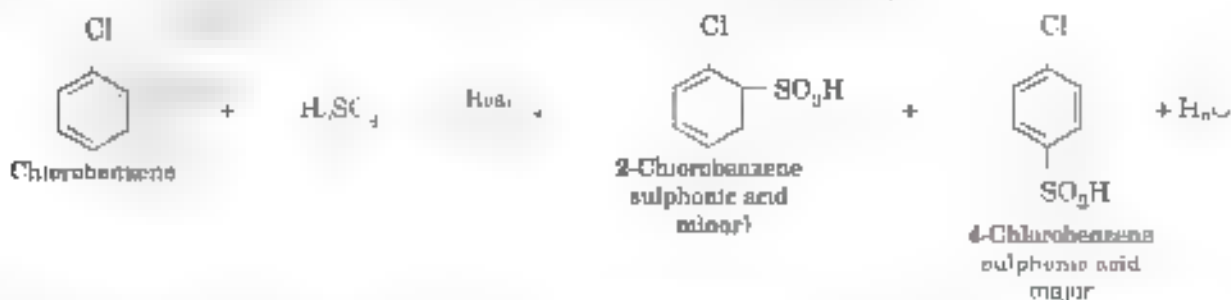
1. **Halogenation.** It takes place by reacting haloarenes with halogens in the presence of ferric salt as catalyst



2. **Nitration.** It is carried out by heating haloarene with conc. HNO_3 in the presence of conc. H_2SO_4 .

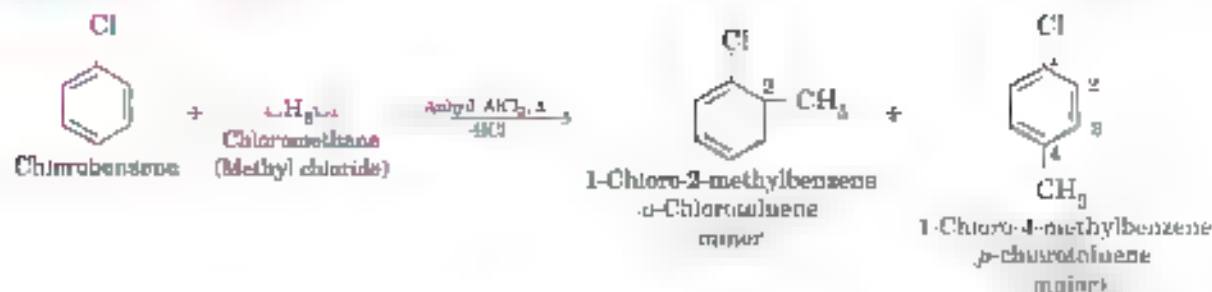


3. **Sulphonation.** It is carried out by heating haloarene with concentrated H_2SO_4 .

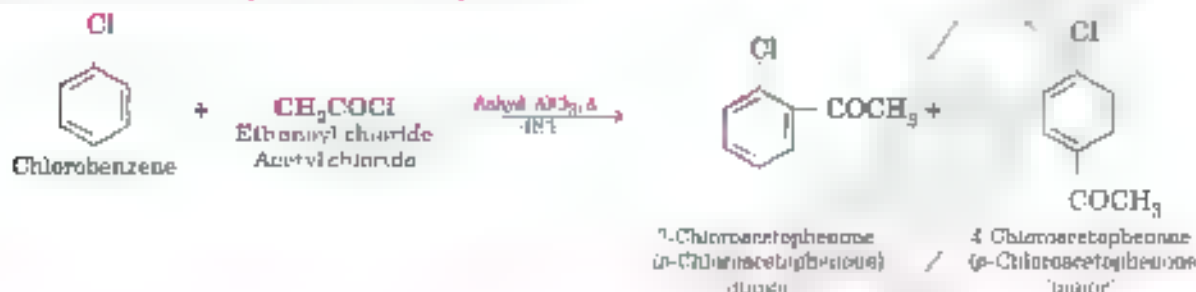


4. **Alkylation and acylation (or alkanoylation).** The reaction known as **Friedel-Crafts reaction** is carried by treating haloarene with alkyl chloride or acyl chloride in the presence of anhydrous aluminium chloride acting as catalyst. For example,

(i) Friedel Crafts alkylation



(ii) Friedel Crafts acylation / alkanoylation



Comparison of reactivity of alkyl, vinyl and aryl halides

Vinyl halides and aryl halides are less reactive than alkyl halides. This is mainly because the vinyl and aryl halides have partial double bond character between carbon and halogen atoms, resulting in a stronger C—X bond. As a result, carbon halogen bond of a vinyl or aryl halide is stronger than that of an alkyl halide and the bond cleavage is difficult. As shown below, the p-orbital of chlorine atom having a lone pair of electrons overlaps with the unhybridised p-orbital of carbon in vinyl and aryl halide, resulting in partial double bond character to C—Cl bond. As a result, C atom becomes firmly attached to Cl atom and cannot be easily substituted.



Alternatively, it may be noted that vinyl halides and aryl halides generally do not undergo $\text{S}_\text{N}1$ or $\text{S}_\text{N}2$ reactions. This is because

- $\text{S}_\text{N}1$ reaction requires ionization to form a vinyl or aryl carbocation. These are less stable than alkyl carbocations. In chlorobenzene and vinyl chloride, the phenyl cation or the vinyl cation formed as a result of self ionization are highly unstable and do not form readily. These will not be stabilized by resonance because the sp^2 -hybridised p-orbital of carbon, bearing positive charge is perpendicular to the p-orbital of the phenyl group or the vinyl group. Therefore, phenyl cation or vinyl cation are not formed and hence $\text{S}_\text{N}1$ mechanism cannot occur.



- $\text{S}_\text{N}2$ reaction requires back side attack by the nucleophile, which is not possible in case of vinyl or aryl halides because of repulsion of the electrons in the double bond or aromatic ring.

Moreover they are unreactive in S_N2 reactions because the carbon-halogen bond of vinylic or phenyl halides is stronger due to double bond character.



However, there is no possibility of double bond character in C-halogen bond in alkyl halides. In benzylic halides also, there is a CH_2 group separating the halogen atom from a sp^3 hybridized carbon. Therefore, the filled p -orbital of halogen atom (e.g. Cl) cannot overlap sideways with the empty hybridized p -orbital of Carbon. Therefore, the C-Cl bond is not very strong and can be easily cleaved. Thus, all alkyl halides and benzylic halides are more reactive than vinyl and aryl halides.



SOLVED EXAMPLES

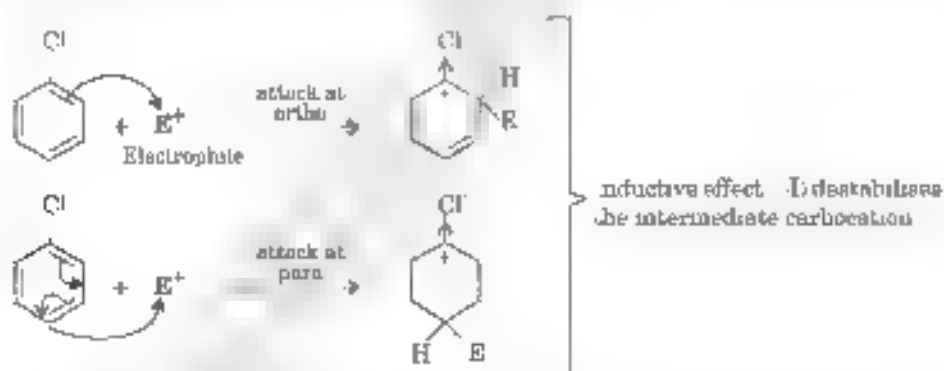
□ Example 20.

Although chlorine is an electron withdrawing group, yet it is ortho-para directing in electrophilic aromatic substitution reactions. Why?

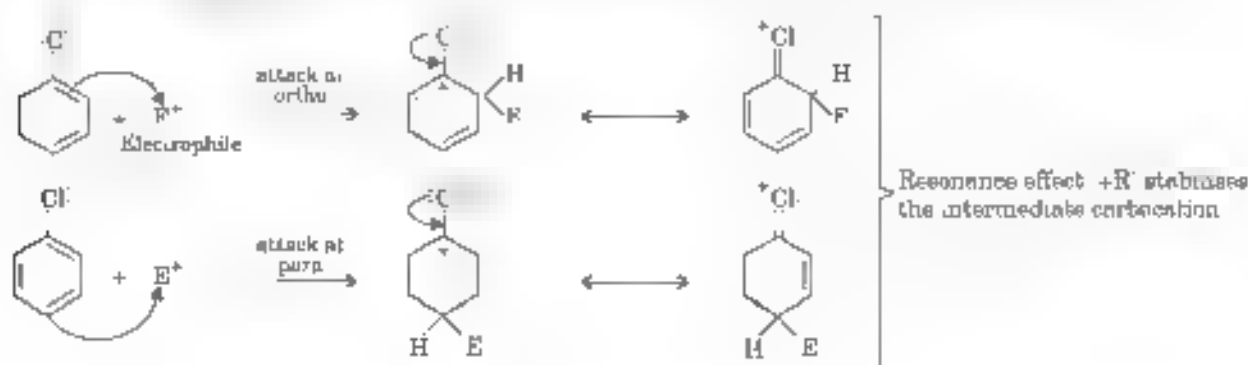
[N.I.E.T.]

Solution.

Chlorine is an electron withdrawing group and has inductive effect. Therefore, it withdraws electrons from the benzene ring and tends to destabilize the intermediate carbocation formed during the electrophilic substitution reaction. The intermediate carbocations for ortho- and para- attacks are shown below.



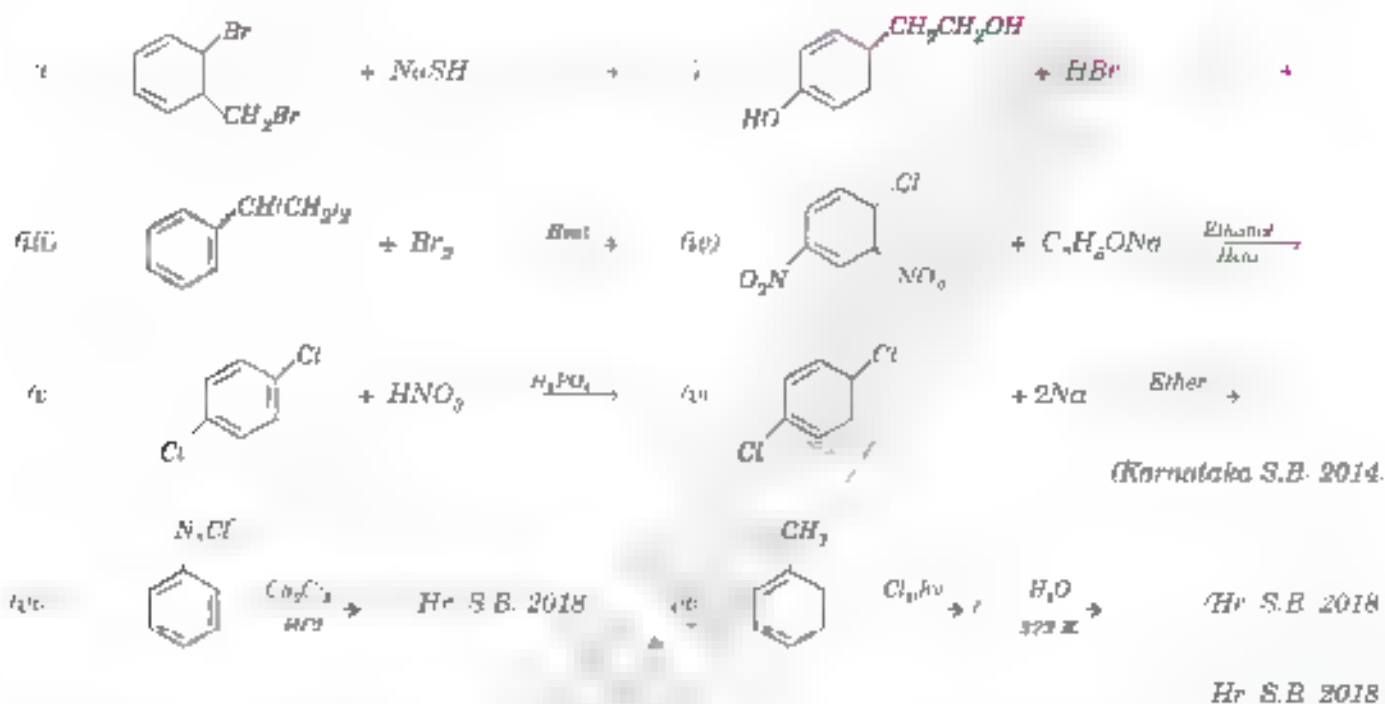
However, the lone pairs of electrons on the chlorine atom stabilise the intermediate carbocation due to resonance.



Since $-I$ effect of Cl is stronger than its $+R$ effect therefore it causes electron withdrawal and thus causes net deactivation. The resonance effect tends to oppose the inductive effect for attack at ortho and para position and hence makes deactivation less for ortho- and para- attack. Thus we can say that the reactivity is controlled by the stronger inductive effect and orientation is controlled by the resonance effect. Thus although chlorobenzene is less reactive than benzene but it is ortho-para directing in electrophilic substitution reaction.

Example 21

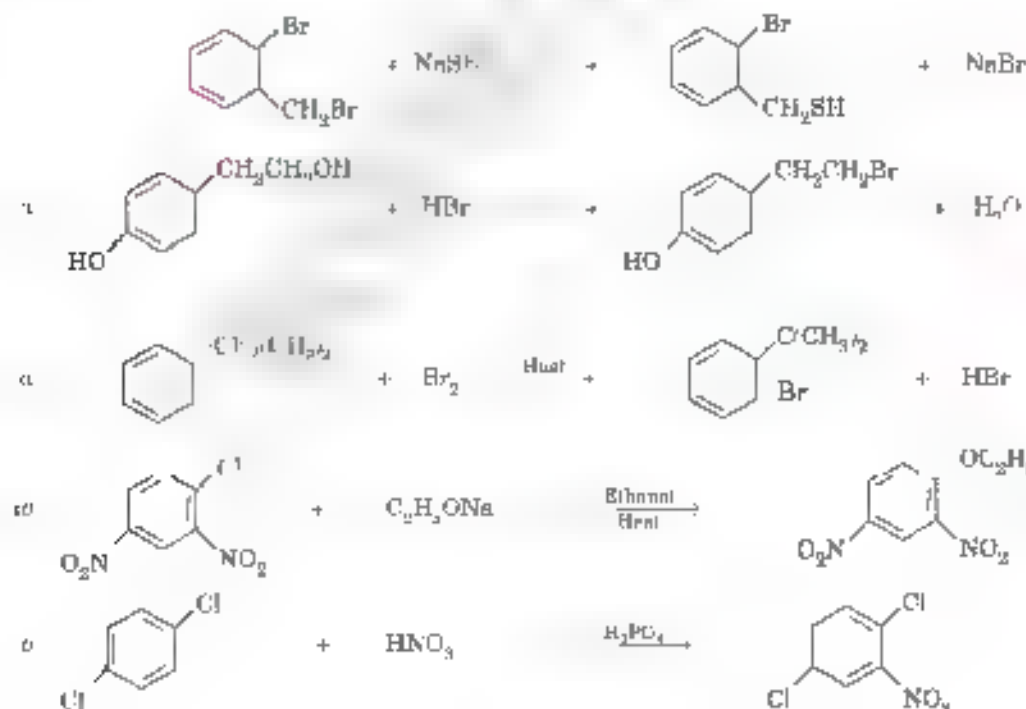
(a) Write the structure of the major product in each of the following



Hr S.B. 2018

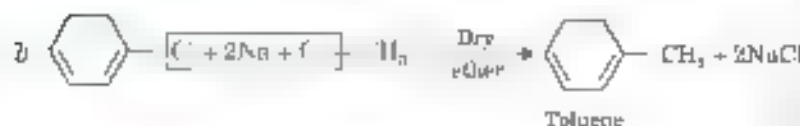
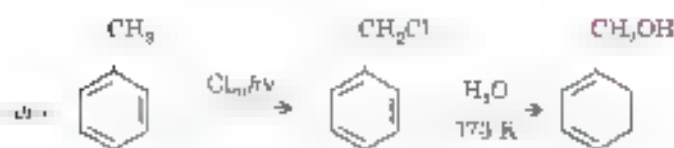
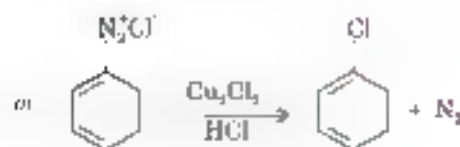
b) Write the structure of the product formed when chlorobenzene is treated with methyl chloride in the presence of sodium metal and dry ether.

Solution: (a)



HELP

Benzyllic $-\text{OH}$ group is readily substituted than aryl $-\text{OH}$ group.

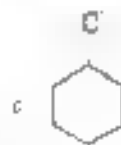
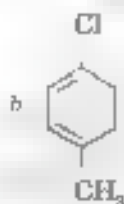
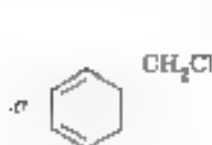


Practice Problems

- Which out of *o*-chloronitrobenzene and 2,4,6-trinitrochlorobenzene is more reactive towards nucleophilic substitution?
- Write the structure of diphenyl. How is it prepared from chlorobenzene?
- Which of the following is an aryl halide?



- Which of the following will be least reactive towards nucleophilic substitution reaction?



- Write the possible isomers of the aromatic compound having molecular formula $\text{C}_7\text{H}_7\text{Cl}$. Which of these will have weakest C—Cl bond?

- Identify X, Y and Z in the following reactions.



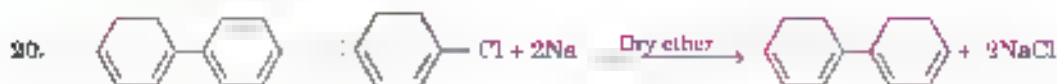
- Give reagents, inorganic or organic compound needed to convert benzyl bromide into

- benzyl iodide
- benzyl ethyl ether
- benzyl alcohol
- benzyl cyanide
- benzyl acetate
- nitromethyl benzene

20. How are nitrofluorobenzene and chlorobenzene sulphonic acid are prepared from chlorobenzene? Uttarakhand S.B. 2019

Answers to Practice Problems

18. 2, 4, 6-trinitrochlorobenzene



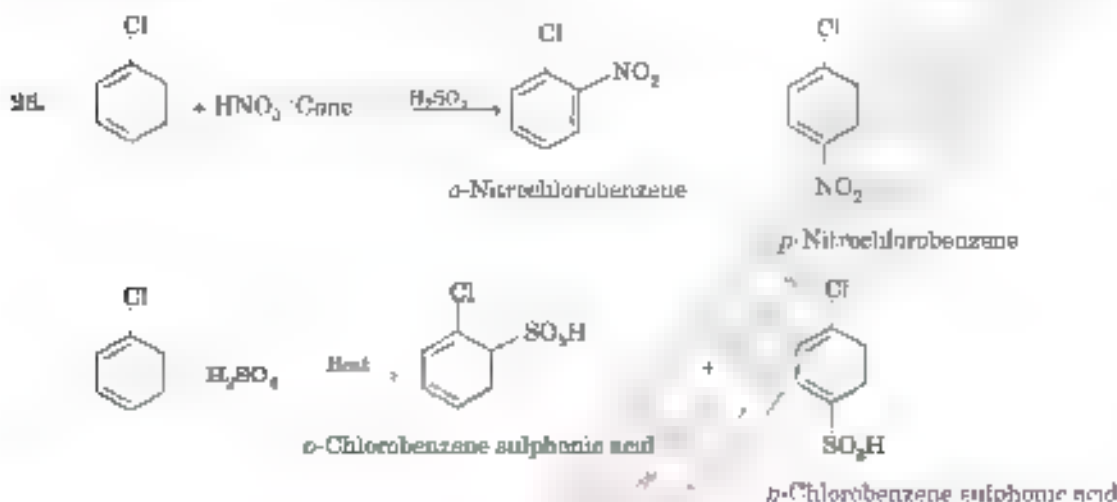
21. (c)

22. (b)

23. Benzyl chloride

24. (a) $C_6H_5N_2^+Cl^-$, C_6H_5Br , C_6H_5OH (b) C_6H_5Cl , C_6H_5CN , C_6H_5COOH
 (c) C_6H_5I , C_6H_6 , C_6H_5 diphenyl

25. (i) NaI (ii) $NaOC_2H_5$
 (iii) NaOH (iv) NaCN
 (v) $NaOOCCH_3$ (vi) $AgNO_3$



SOME COMMERCIALY IMPORTANT COMPOUNDS

Carbon compounds containing more than one halogen atoms are called **polyhalogen compounds**. These compounds are useful in industry and agriculture. The uses and environmental effects of some polyhalogens are discussed below

1. Dichloromethane (methylene chloride), CH_2Cl_2

Methylene chloride is a colourless, sweet smelling liquid. It is a volatile liquid having low boiling point of 313 K and its specific gravity is 1.37

Uses. (i) It is used as a solvent in a paint remover and also as a metal cleaning and finishing solvent.

Because of its low boiling point and low inflammability it is an effective solvent for extraction in pharmaceutical in the manufacturing of drugs and food industries

(ii) It is also used as a propellant in aerosols.

(iv) It is used as refrigerant and dewaxing agent.

Methylene chloride is known to have **harmful effects** on the human central nervous system. Exposure to low levels of methylene chloride in air can lead to slightly impaired hearing and vision. However exposure to high levels of methylene chloride can cause dizziness, nausea, tingling and numbness in the fingers and the toes. Moreover in humans direct contact of methylene chloride with skin causes intense burning and mild redness of the skin. Direct contact with the eyes can even burn the cornea. It was observed that the cornea of animals was damaged when exposed to vapours of methylene chloride.

2. Trichloromethane $CHCl_3$ (Chloroform)

Chloroform is prepared in the laboratory by distilling a mixture of ethanol with a suspension of bleaching powder



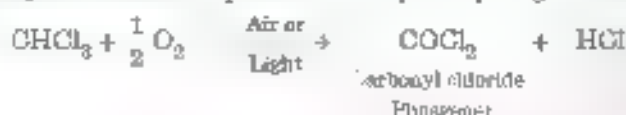


It can also be prepared by distilling acetone with bleaching powder as



It is a colourless oily liquid with a peculiar sickly smell and a burning taste. It is heavier than water. It is sparingly soluble in water but readily soluble in organic solvents such as ethanol and ether. It is a poisonous compound. The vapour when inhaled causes unconsciousness. Due to this reason, chloroform is used as an **anaesthetic**.

Chloroform is slowly oxidised into a poisonous compound **phosgene** (carbonyl chloride) in the presence of air or light



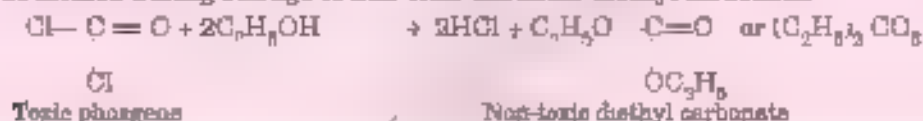
Since phosgene is very poisonous, its presence makes chloroform *unsafe for use as anaesthetic*.

Preservation of chloroform Since chloroform is used for anaesthetic purposes, therefore, its slow oxidation to phosgene must be prevented. The following **precautions** are taken to keep chloroform pure

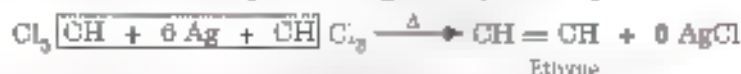
(i) It is stored in dark coloured bottles to protect it from sunlight

The bottles containing chloroform are completely filled up to brim and are properly stoppered to keep out air

(ii) A small amount of 10% alcohol is added to the bottles of chloroform. This reacts with phosgene that may be formed during storage to form a non-toxic non-volatile diethyl carbonate.



Chloroform reacts with silver powder to give ethyne (acetylene),



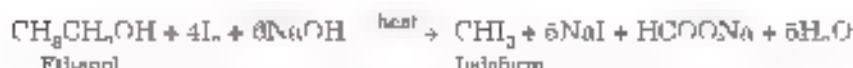
Uses of chloroform. Chloroform has the following uses

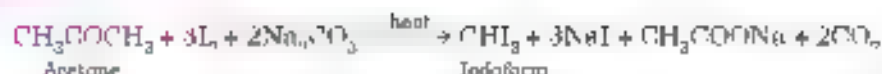
- In industry chloroform is used as an important solvent particularly for fats, alkaloids, iodine, waxes, rubber, etc.
- It is used as an anaesthetic. But these days it has been replaced by other anaesthetics such as ether, it is very toxic in nature.
- It is used as a laboratory reagent.
- It is used in the preparation of chloropicrin, chloroform, etc.
- It is used in medicines.
- It is used in the production of freon refrigerant, R-22

In the earlier days, chloroform was used as a general anaesthetic in surgery. This is because inhaling chloroform vapour depresses the central nervous system. It has been observed that breathing about 900 parts of chloroform per million parts of air (900 ppm) for a short time causes dizziness, fatigue and headache. Chronic chloroform exposure may damage liver and kidneys because chloroform is metabolised to poisonous phosgene. Some people develop sores when the skin is immersed in chloroform. Therefore, the use of chloroform as an anaesthetic has been replaced by less toxic and safer anaesthetic such as ether.

3. Iodoform (Tri-iodomethane) CHI_3

Iodoform is prepared in the laboratory by heating ethanol or acetone with iodine and Na_2CO_3 or alkali solution





Iodoform: is a yellow coloured crystalline solid with m.p. 382 K having characteristic or pleasant odour.

It is insoluble in water but readily dissolves in ethyl alcohol and ether. It has an antiseptic action due to liberation of free iodine.

Uses of Iodoform. The important uses of Iodoform are

1. It is used as an antiseptic and this nature is due to free iodine that it liberates and not due to Iodoform itself. However, because of its very unpleasant smell, it has now been replaced by other formulations containing iodine.
2. It is used in the manufacture of pharmaceuticals.

4. Tetrachloromethane (Carbon tetrachloride) CCl_4

Carbon tetrachloride is a colourless oily liquid with sickly smell. It is insoluble in water but is soluble in organic solvents such as ether, alcohol. Its boiling point is 350 K. It is inflammable.

Uses. The important uses of CCl_4 are

1. It is used in large quantities in the manufacture of refrigerants and propellants for aerosol cans.
2. It is used as a feedstock in the synthesis of chlorofluorocarbons, freons and other chemicals.
3. It is used as a solvent for the manufacture of pharmaceuticals.
4. It is used as a solvent for oils, fats, waxes, etc.
5. It is used as a fire extinguisher under the name **pyrene**.
6. It is used in dry cleaning.

Until the mid 1980s, carbon tetrachloride was widely used as a cleaning fluid, both in industry as a degreasing agent and at the home, as a spot remover and as a fire extinguisher under the name pyrene. However, it was observed that exposure to carbon tetrachloride causes liver cancer in animals. The most common effects are dizziness, high, headache, nausea and vomiting which can cause permanent damage to nerve cells. In severe cases these effects can lead rapidly to stupor, laziness, coma, unconsciousness or even death.

Exposure to carbon tetrachloride vapours can make heart beat irregularly or even, may stop it. When brought in contact with eyes, it may cause irritation in eyes.

It has also damaging effects on environment. When carbon tetrachloride is released into air, it rises to the atmosphere and depletes the ozone layer. Depletion of the ozone layer increases the human exposure to ultraviolet radiations which may lead to increased skin cancer, eye diseases, etc. and possible disruption of the immune system.

5. Freons

The chloro-fluoro compounds of methane and ethane are collectively known as **freons**. These are extremely stable, low boiling, non-inflammable, non-toxic, non-corrosive, easily liquefiable and highly unreactive compounds. They are stable even under high pressures and temperatures and therefore, find use as refrigerants. Among these dichlorodifluoromethane CCl_2F_2 known as Freon-12 is the most important compound of this class because of its industrial uses. It is manufactured by the action of antimony fluoride on carbon tetrachloride in the presence of antimony pentachloride by **Swarts reaction**.



Alternatively, it may be prepared by the action of hydrogen fluoride on carbon tetrachloride in the presence of carbon and ferric chloride.



Uses

Freons are used as refrigerants in refrigerators and air conditioners and hence is the name freons.

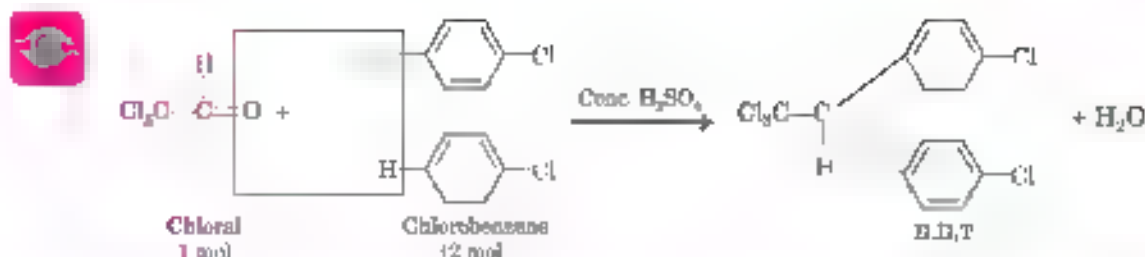
These have also been used extensively as propellants for aerosols and foams, i.e. spray out deodorants, cleaners, shaving creams, hair sprays and insecticides.

However, freons are persistent, because micro organisms and other agents that cause biodegradation of natural organic materials are unable to break these stable molecules or can do so only extremely slowly. Therefore, most freon eventually makes its way into the atmosphere where it diffuses unchanged into the stratosphere. In stratosphere, freons undergo photochemical decomposition and initiate radical chain reactions and deplete the protective ozone layer surrounding our earth. Therefore, the use of freons as propellants and refrigerants has been drastically discouraged. It has also been banned in many countries.

6. DDT 2, 2-bis (p-chlorophenyl) 1, 1, 1 Trichloroethane or p, p'-Dichlorodiphenyl trichloroethane

DDT was first prepared in 1873 but it was not until 1939 when Paul Muller, at Geigy pharmaceuticals in Switzerland, discovered the effectiveness of DDT as an insecticide. Paul Muller was awarded Noble Prize in Medicine and Physiology in 1948 for this discovery.

It is synthesised by treating a mixture of chloral (alcohol) with chlorobenzene in the presence of concentrated H_2SO_4 .



DDT is almost insoluble in water but it is moderately soluble in polar solvents. DDT is a powerful insecticide. It is widely used as an insecticide for killing mosquitoes and other insects.

Side Effects of DDT. DDT is one of the most powerful and effective insecticides. The use of DDT increased enormously after world war II because of its effectiveness against the mosquito that spreads malaria and other fatal diseases. However, the excessive use of DDT leads to the development of insects with resistance to DDT and also DDT was found to have high toxicity towards fish. The chemical stability of DDT and its fat solubility further worsened the problem. DDT is non-biodegradable. Its residues were present in the environment and its long term effects could be highly dangerous. DDT is not metabolised very rapidly by animals rather it gets deposited and stored in fatty tissues. This raised alarming dangers. Therefore, its use has been banned in U.S.A. in 1973. However, in spite of its dangerous side effects, DDT is still being widely used in India and other Asian countries due to non-availability of other cheaper insecticides.

ANALYSIS AND DIFFERENCES BETWEEN HALOALKANES AND HALOARENES

The main difference between haloalkanes and haloarenes is :

Haloalkane	Haloarene
The halogen atom in haloalkanes is very reactive and can be easily replaced by nucleophiles such as OH^- , NH_3 , CN^- , SH^- etc.	The halogens on haloarenes are strongly held to the nucleus and therefore, it cannot be easily replaced by nucleophiles.

The haloalkanes and haloarenes can be distinguished by the following tests:

1 Silver nitrate test. In this test, the halide is warmed with aqueous or alcoholic KOH . The solution is then acidified with dil. HNO_3 and AgNO_3 solution is added.

If precipitate occurs, it indicates alkyl, benzyl or aryl halides.

If precipitate does not occur, it indicates aryl or vinyl halides.

It may be noted that the precipitate formed should be soluble in dil. HNO_3 .

2. Lassaigne's test. This test is performed to identify the halogen atom present in the compound. In this test, Lassaigne's solution is prepared by heating the compound with sodium metal. The Lassaigne solution is boiled with dil. HNO_3 to expel the gases if evolved. Then add AgNO_3 solution to the resulting solution.

White ppt soluble in NH_4OH indicates the presence of chloride. Light yellow ppt partially soluble in NH_4OH indicates bromide. Dark yellow ppt insoluble in NH_4OH indicates iodide.

Practice Problems

- In each of the following pairs of compounds, which will give iodoform test ?
 - Sec-butyl alcohol and tert-butyl alcohol
 - Ethyl alcohol and isopropyl alcohol
 - Formaldehyde and acetaldehyde
 - Methylpropyl ketone and diethyl ketone
- How will you distinguish between ethyl chloride and vinyl chloride ?
- Mention the products obtained when chloroform reacts with (a) acetic acid (b) silver powder (c) ammonia in the presence of alcoholic KOH (d) acetone
- Complete the following reactions
 - $\text{CHCl}_3 + 2\text{H} \xrightarrow{\text{Zn, HCl}}$
 - $\text{CCl}_4 + \text{H}_2\text{O} \rightarrow$
 - $\text{CHCl}_3 + \text{CH}_3\text{NH}_2 + 3\text{KOH} \rightarrow$
 - $\text{CH}_3\text{CH}_2\text{OH} + \text{I}_2 + \text{NaOH} \rightarrow$
 - $\text{CHCl}_3 + \text{O}_2 \xrightarrow{\text{Sunlight}}$
- Write the IUPAC names of isomers of $\text{C}_4\text{H}_9\text{Cl}$. Give one test to distinguish these.

Answers to Practice Problems

28. Ethyl chloride reacts with acetic acid AgNO_3 solution to give white ppt of AgCl whereas vinyl chloride does not react.



29. a) Chloropicrin b) Acetylene c) Phenyl isocyanide d) Chlorotons
31. 1, 2-Dichloroethane. 1, 1-Dichloroethane Hydrolysis of 1, 2-Dichloroethane with aqueous NaOH gives ethylene glycol while the hydrolysis of 1, 1-Dichloroethane gives ethanol.

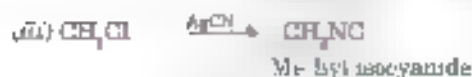
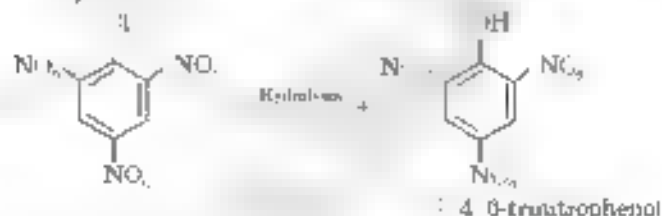
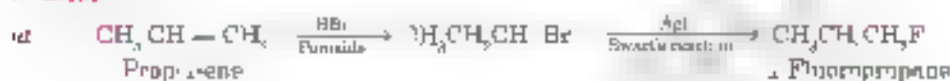
SOLVED EXAMPLES

□ **Example 22.**

- (a) How would you convert the following
 (i) Prop-1-ene to 1-fluoropropane
 (ii) Chlorobenzene to 2-chlorotoluene
- (b) Write the main products when
 (i) n-butyl chloride is treated with alcoholic KOH.
 (ii) 2, 4, 6-trinitrochlorobenzene is subjected to hydrolysis
 (iii) methyl chloride is treated with AgCN.

A.I.S.B 2015

Appendix



 Example 23.

- d Draw the structure of the major monohalogeno products in each of the following reactions.



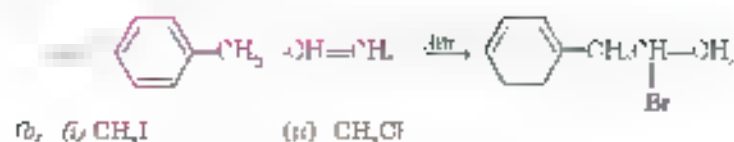
- b Which halogen compound in each of the following pairs will react faster in S_N2 reactions.

- $$(ii) (CH_3)_3C-Cl \text{ or } (CH_3)_3C-$$

A.I.S.E. 2014

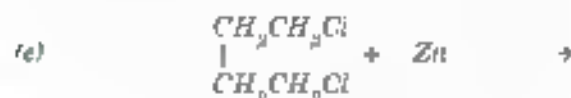
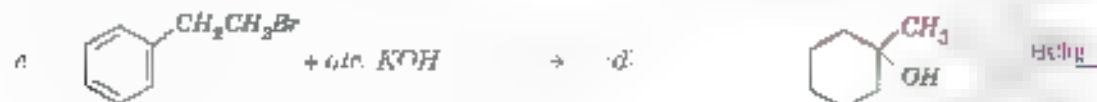
Solution :



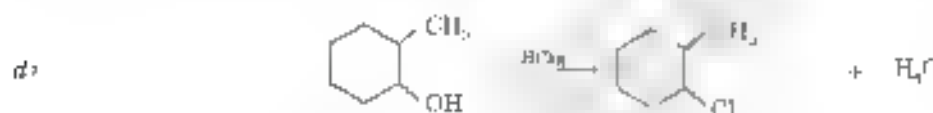


Example 24.

Write the product or products for each of the following reactions



Solution

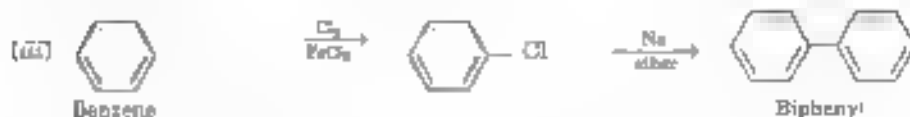
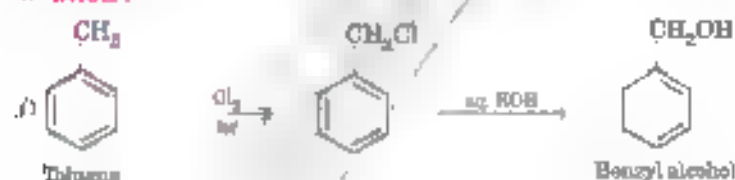


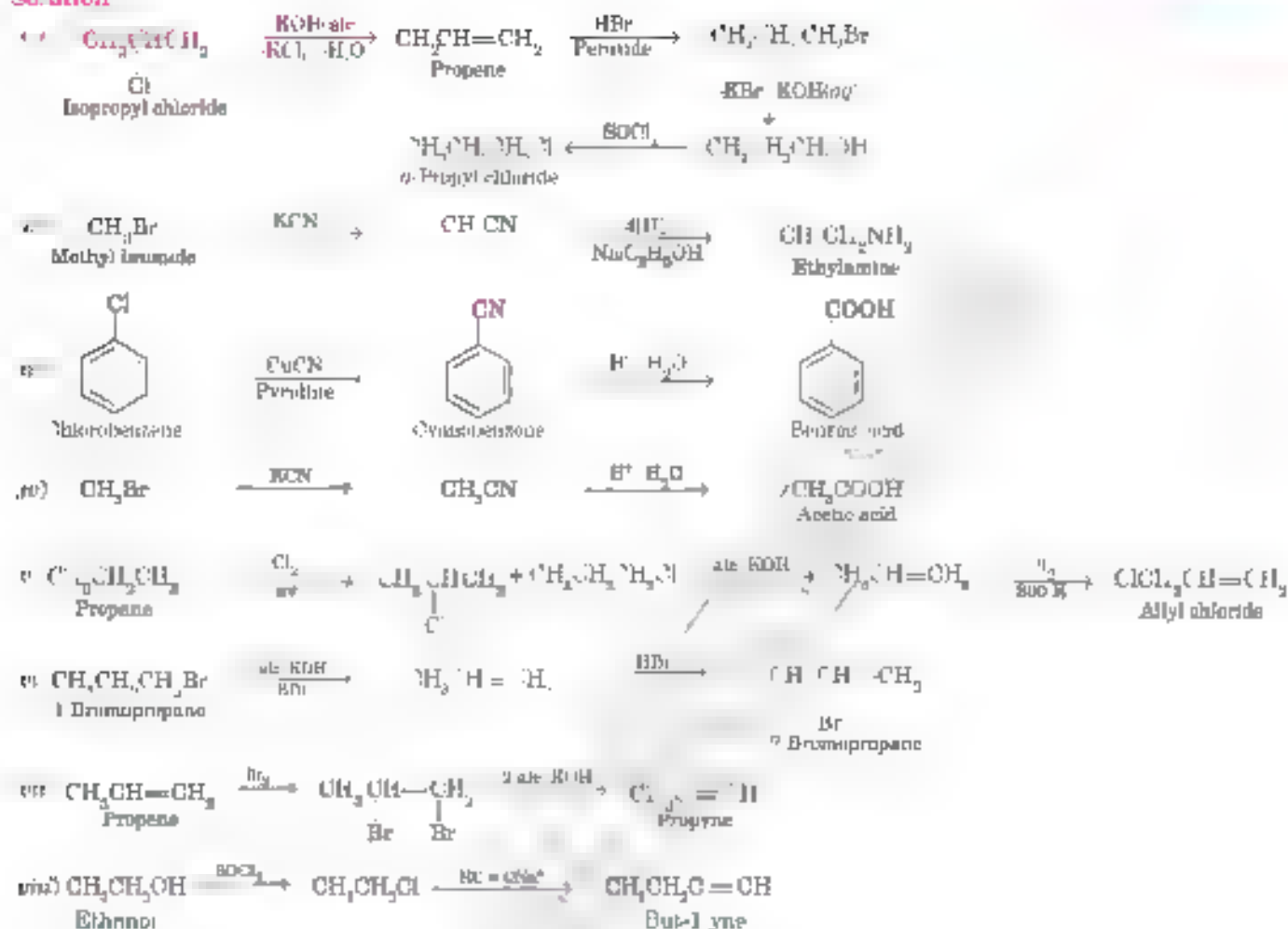
Example 25.

How would you carry out the following conversions in not more than two steps

- (i) Toluene to benzyl alcohol (ii) Ethanol to ethyl fluoride (iii) Benzene to biphenyl
(iv) 1-Chlorobutane to n-octane (v) Benzyl alcohol to phenylethanol (vi) But-1-ene to But-2-ene

Solution:



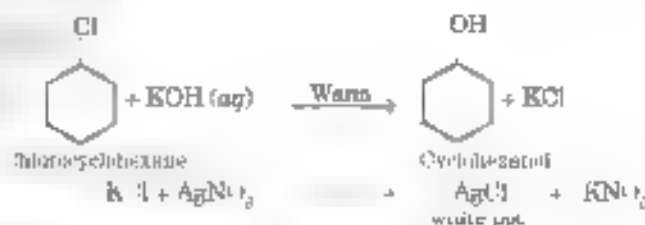
Solution**Example 80.**

How are you distinguish between the following pairs of compounds and test.

- a) Chlorobenzene and chlorocyclohexane b) Chlorobenzene and benzyl chloride
 c) Ethyl chloride and vinyl chloride d) Chlorobenzene and t-butyl chloride
 e) Chloroethane and bromoethane f) 2-Bromopropane and 1-bromopropane.

Solution: (a) Chlorobenzene and chlorocyclohexane Add a small quantity of aqueous KOH to each compound. Acidify with dil. HNO_3 and add silver nitrate solution.

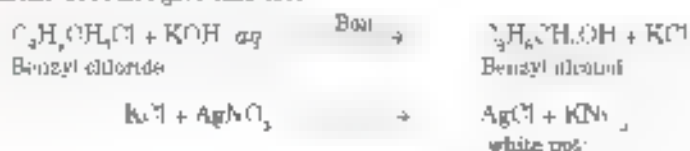
Chlorocyclohexane when heated with aq. KOH undergoes hydrolysis to give potassium chloride. Potassium chloride reacts with silver nitrate to give white ppt. of AgCl.



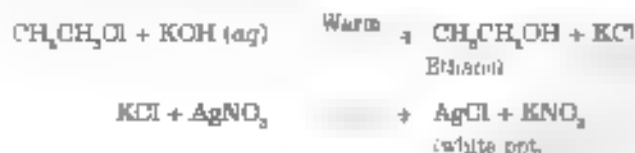
Chlorobenzene does not undergo hydrolysis under these conditions to produce phenol and KCl with aq. KOH. Therefore, it does not give white ppt.



(b) **Chlorobenzene and benzyl chloride** Same as (a). Benzyl chloride reacts with alcoholic AgNO_3 solution to give white ppt of AgCl while chlorobenzene does not give this test.

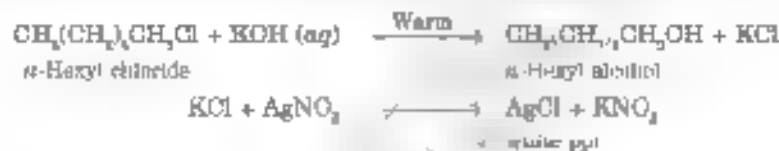


(c) **Ethyl chloride ($\text{C}_2\text{H}_5\text{Cl}$) and vinyl chloride ($\text{CH}_2=\text{CHCl}$)** Ethyl chloride reacts with a solution AgNO_3 solution to give white ppt of AgCl while vinyl chloride does not give this test.

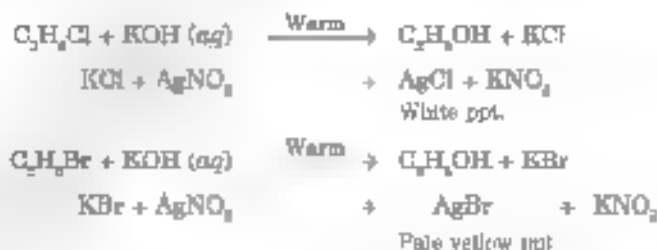


This is because alkyl halides ($\text{C}_2\text{H}_5\text{Cl}$) are more reactive than vinyl halides.

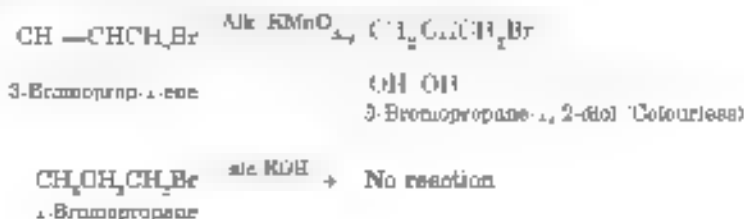
(d) **Chlorobenzene and *n*-hexyl chloride** Same as (a). *n*-Hexyl chloride is a haloalkane and gives white ppt in this test. In contrast chlorobenzene is aryl halide and does not give white ppt in this test.



(e) **Chloroethane and bromoethane** Add a small amount of aqueous $\text{K}_2\text{Cr}_2\text{O}_7$ in each compound. Acidify with dil. HNO_3 and add a few drops of AgNO_3 solution. A white ppt (Aq. sol. insoluble in NH_4OH) indicates chloroethane while light yellow ppt AgBr partially soluble in NH_4OH indicates bromoethane.



(f) **2-Bromopropene (allyl bromide) and 1-bromopropane (alkyl bromide)** Add a small amount of dil. alkaline KMnO_4 solution (Bayer's reagent) to each compound and shake. 2-Bromopropene ($\text{CH}_2=\text{CHCH}_2\text{Br}$) decolorises pink colour of KMnO_4 while 1-bromopropane ($\text{CH}_3\text{CH}_2\text{CH}_2\text{Br}$) does not.



add on

Conceptual Questions

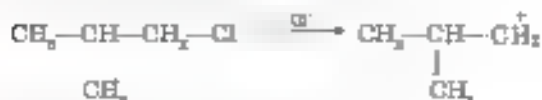
- Q.1 Out of $\text{CH}_3-\underset{\text{CH}_3}{\text{CH}}-\text{CH}_2-\text{Cl}$ and $\text{CH}_3-\text{CH}_2-\underset{\text{CH}_3}{\text{CH}}-\text{Cl}$, which is more reactive towards $\text{S}_{\text{N}}1$

reaction and why?

(D.S.B. 2016)

Ans. $\text{CH}_3-\text{CH}_2-\underset{\text{CH}_3}{\text{CH}}-\text{Cl}$ is more reactive

The $\text{S}_{\text{N}}1$ reaction proceeds through the formation of carbocation. The compound which forms more stable carbocation will be more reactive



1-Chloro-2-methylpropane

1° Carbocation

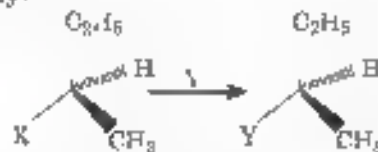
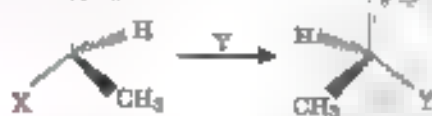


2-Chlorobutane

2° Carbocation

Since 2° carbocation is more stable than 1° carbocation, 2-chlorobutane will be more reactive towards $\text{S}_{\text{N}}1$ reaction.

- Q.2 Which of the following two reactions is $\text{S}_{\text{N}}2$ and why?

(i) C_2H_5 (ii) C_2H_5 

A.I.S.B. 2016

Ans. Reaction (i) is $\text{S}_{\text{N}}2$ because it proceeds by inversion of configuration

- Q.3 Chloroform contains chlorine but gives no reaction with AgNO_3 solution. Why?

Ans. CHCl_3 contains chlorine but it is bonded to carbon by covalent bond and therefore, it is not in ionic form. Hence, it does not combine with AgNO_3 solution.



- Q.2. Out of HCl (g) and SOCl_2 , which is preferred for converting ethanol into chloroethane?

Ans. SOCl_2 is preferred because in this case both the other products formed are gases SO_2 and HCl and escape readily leaving behind pure chloroethane



The second reaction is generally carried out in the presence of dehydrating agent such as anhydrous ZnCl_2 .

- Q.6. Why is chloroform stored in dark coloured bottles?

H.P.S.B. 2015

Ans. Chloroform is oxidised to poisonous phosgene in the presence of air as



Therefore, to protect it from light chloroform is stored in dark coloured bottles.

- Q.6. Haloarenes are insoluble in water but are soluble in benzene. Explain.

Pb.S.B. 2015, H.P.S.B. 2015

Ans. Haloarenes are insoluble in water because they cannot form hydrogen bonds with water molecules. However, these are soluble in benzene in accordance with the general principle of solubility i.e. like dissolves like. Haloarenes are organic compounds having a large hydrocarbon part (benzene ring) and are soluble in hydrocarbon solvents like benzene.

- Q.7. The *p*-isomer of dichlorobenzene has higher melting point than *o*- and *m*-isomer. Why?

Pb.S.B. 2015

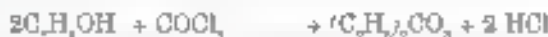
Ans. The melting point of para isomer is quite higher than that of ortho or meta isomers. This is due to the fact that *p* has symmetrical structure and therefore, its molecules can pack closely in crystal lattice. As a result, intermolecular forces of attraction are stronger and therefore greater energy is required to break the lattice and it melts at higher temperature.

Q.9. Iodoform gives a precipitate with silver nitrate on heating while chloroform does not.

Ans. Carbon-iodine bond is quite weak ($213.4 \text{ kJ mol}^{-1}$) as compared to carbon-chlorine bond ($331.4 \text{ kJ mol}^{-1}$). Therefore, when iodoform is heated with AgNO_3 solution, C-I bond gets cleaved easily and iodide ions react with AgNO_3 solution to give precipitate of AgI . On the other hand, C-Cl bond does not get cleaved.

Q.10. A small amount of ethyl alcohol is usually added to chloroform bottles. Why?

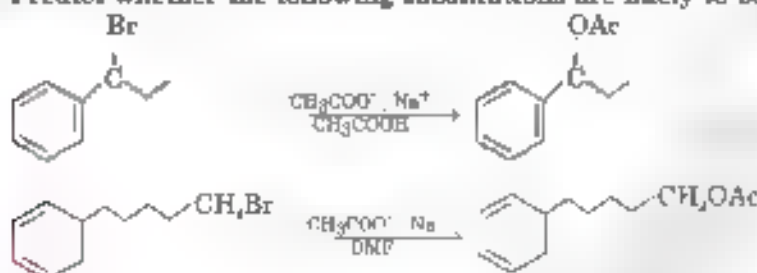
Ans. Alcohol retards the oxidation of chloroform to phosgene and it converts phosgene (any formed) to harmless ethyl carbonate.



Q.10. Organic halogen compounds used in industry as solvents are chlorides rather than bromides and iodides. Explain.

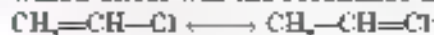
Ans. Organic alkyl chlorides are used in industry as solvent because chlorides are more volatile than bromides and iodides.

Q.1.1. Predict whether the following substitutions are likely to be S_N1 or S_N2 .



Ans. (i) S_N1 (because benzylic and secondary) (ii) S_N2 (primary)

Q.12. Which effect will the resonance have on the dipole moment of vinyl chloride?



Ans. It will increase its dipole moment.

Q.18. Why is vinyl chloride less reactive than ethyl chloride?

Ans. In vinyl chloride, the electron pair on chlorine atom conjugates with the π electron pair of the double bond.

$$\text{CH}_2=\text{CH}-\text{Cl} \longleftrightarrow \text{CH}_2^--\text{CH}=\text{Cl}^+$$


As a result there is partial double bond character in C-Cl and its bond strength increases. Consequently it becomes difficult to cleave C-Cl bond as compared to the bond in ethyl chloride where no such conjugation is possible.

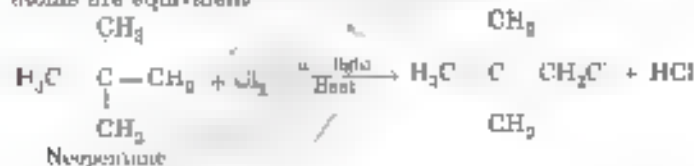
Q 14. The use of chloroform as an anaesthetic is decreasing. Why?

(J.P.S.B. 2015)

Ans. Because in some cases, CHCl_3 causes cardiac and respiratory problems. Therefore, its use as an anesthetic is decreasing.

Q.15. A hydrocarbon C_4H_{10} gives only one chlorination product. Identify the compound.

Ans. The hydrocarbon which gives monochloro derivative only is neopentane because in it all the hydrogen atoms are equivalent.



Q.16. Give the IUPAC name of the product formed when

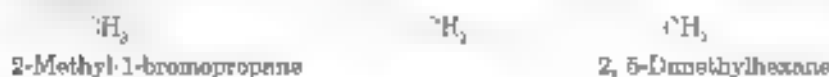
(i) 2-Methyl 1-bromopropane is treated with sodium in the presence of dry ether.

(iv) 1-Methylcyclohexene is treated with HCl .

iii. Chloroethane is treated with silver nitrate.

JEL Sample Paper 2017 18

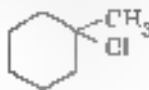
Ann. $\text{C}_{10}\text{H}_{16}\text{Br} + 2\text{NH}_3 \rightarrow \text{C}_{10}\text{H}_{18} + \text{Br}^-\text{NH}_4^+$



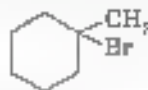
Q.17 Predict the order of reactivity of the following compounds in S_N1 reactions



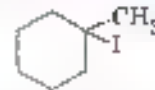
(i)



(ii)



(iii)



(iv)

Ans. (i) is secondary halide and other three are tertiary halides. Therefore (iii) will be least reactive. Comparing (i) (ii) and (iv) we know that reactivity increases as chloride < bromide < iodide. Thus the compounds can be arranged in increasing order of reactivity as (i) < (ii) < (iv).

Q.18 Which of the following two compounds would react faster by S_N2 path way : 1-bromobutane or 2-bromobutane and why ? (CBSE Sample Paper 2007)

Ans. 1-bromobutane will react faster than 2-bromobutane by S_N2 path because 1-bromobutane has less steric hindrance in the transition state.

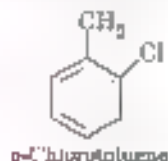
Q.19 Allyl chloride is more reactive than n-propyl chloride towards nucleophilic substitution reaction. Explain why ? (CBSE Sample Paper 2007)

Ans. Allyl chloride is more reactive than propyl chloride towards nucleophilic substitution reaction. This is because of greater stabilization of allylic carbocation intermediate formed by resonance.

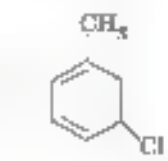


Q.20 Write the various possible isomers of $\text{C}_7\text{H}_7\text{Cl}$ containing benzene ring. Which of these has weakest C—Cl bond.

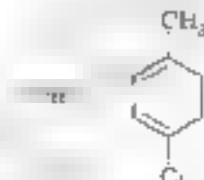
Ans. Four isomers are possible. These are



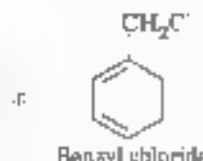
o-Chlorotoluene



m-Chlorotoluene



p-Chlorotoluene



Benzyl chloride

Out of these benzyl chloride (IV) has the weakest C—Cl bond.

Q.21 An alkyl halide with molecular formula $\text{C}_4\text{H}_9\text{Br}$ is optically active. What is its structure ? (P.T.S.B. 2006)

Ans. $\text{CH}_3-\text{CH}(\text{Br})-\text{CH}_2-\text{CH}_3$

Q.22 Which out of the two 2-bromocyclopentanol or 2-cyclopentanol has chiral centre.

Ans.



2-Cyclopentanol



2-Bromocyclopentanol

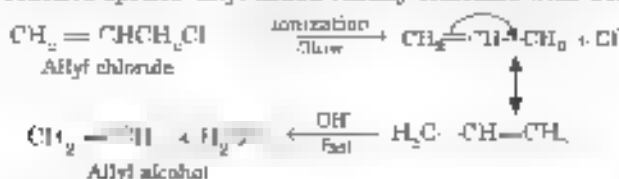
2-Cyclopentanol has a chiral centre.

Q.23 Which of the two $\text{CH}_3\text{CH}=\text{CHCH}_2\text{Br}$ or $\text{CH}_3\text{CHCH}=\text{CH}_2$ is achiral and chiral.

Ans. $\text{CH}_3\text{CH}=\text{CHCH}_2\text{Br}$ is achiral because it does not contain chiral carbon atom. $\text{CH}_3\text{CH}(\text{Br})\text{CH}=\text{CH}_2$ is chiral because it contains chiral carbon atom.

Q.24 Allyl chloride is hydrolysed more readily than n-propyl chloride.

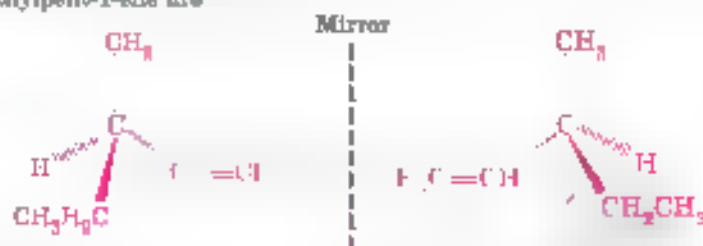
Ans. Allyl chloride readily undergoes ionization to form resonance stabilised carbocation. Since carbocations are reactive species allyl cation readily combines with OH^- ions to form allyl alcohol.



However n-propyl chloride does not undergo ionization to form n-propyl carbocation and hence it gets hydrolysed less readily than allyl chloride.

Q.25. What are enantiomers? Draw the structures of the possible enantiomers of 3-methylpent-1-ene. (D.S.B. 2006)

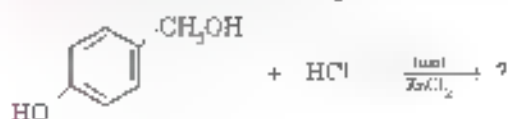
Ans. Stereoisomers which are non superimposable mirror images of each other are called enantiomers. The enantiomers of 3-methylpent-1-ene are



Q.26. Which will have a higher boiling point 1-chloroethane or 2-methyl-2-chlorobutane? Give reasons. (C.B.S.E. Sample Paper 2007)

Ans. 2-Methyl-2-chlorobutane has higher boiling point than 1-chlorobutane because with increase in size of alkyl group, boiling point increases.

Q.27. Write the structure of major monohalo product of the following reaction:



(Meghalaya S.B. 2017)



Q.28. Account for following:

(a) Use of DDT was banned in United States in 1973.

(b) Benzylic halides show high reactivity towards S_N1 reaction. (CBSE Sample Paper 2011)

Ans. a Because of chemical stability of DDT and its fat solubility, it is not metabolized very rapidly by animals. Rather, it gets deposited and stored in fatty tissues. This caused alarming danger due to its toxic effects. Therefore its use has been banned in USA.

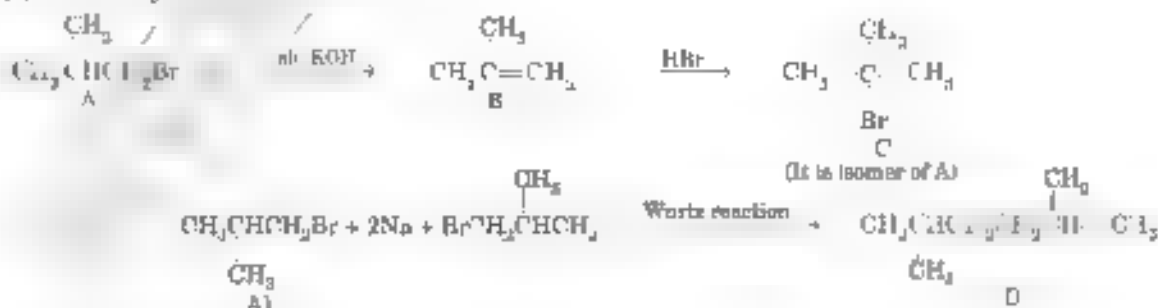
b Benzylic halides show high reactivity towards S_N1 reactions because benzylic carbocation formed is highly stable through resonance.

Q.29. Iodoform has antiseptic properties. Give one reason to support this.

Ans. Iodoform has antiseptic properties due to free liberated iodine.

Q.30. A primary alkyl halide (A), C_4H_9Br reacted with hot alcoholic KOH to give compound (B). Compound (B) reacted with HBr to give (C), which is an isomer of (A). When (A) was reacted with sodium metal, it gave a compound (D), C_8H_{18} which was different than the compound when n-butyl bromide was reacted with sodium. Give the structural formula of (A) and write equations for all the reactions.

Ans. (A) is iso-butylbromide. The reactions are



Q.31. Optically active 2-iodobutane on treatment with NaI in acetone gives a product which does not show optical activity. Explain.

Ans. The reaction of optically active 2-iodobutane with NaI in acetone follows S_N1 mechanism and leads to the formation of equal amounts of the two enantiomers. Thus a racemic mixture is obtained which does not show optical activity.

Q.32. Identify (X) and (Y) in the following: $C_2H_5CH_2CH_2Br$



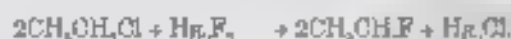
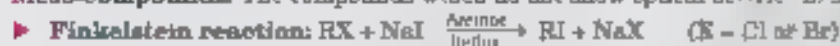
Ans. X $CH_3CH=CH_2$

Y $CH_3CH_2CH_2OH$

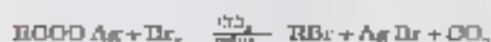
(Tripura S.B. 2016)

Key Terms & Name Reactions

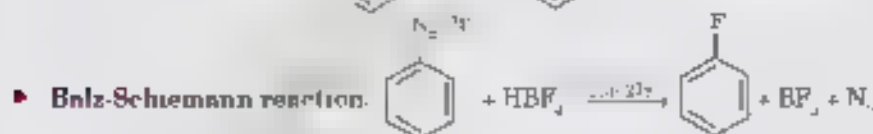
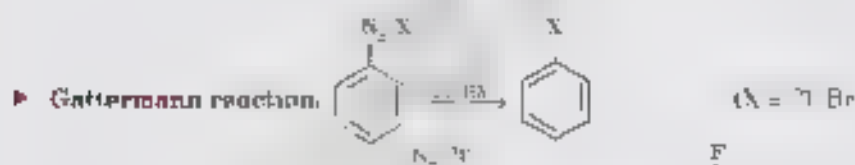
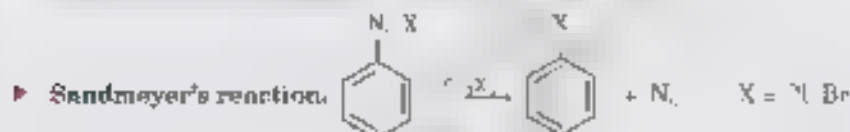
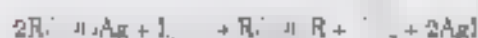
- **Ambident nucleophiles.** The nucleophiles which have more than one site through which the reaction can occur.
- **Optical activity.** The property of a substance to rotate the plane of polarized light.
- **Chiral.** The objects which are non-superimposable on their mirror images.
- **Chirality.** The property of non-superimposability on its mirror image.
- **Achiral.** The objects which are superimposable on their mirror images.
- **Chiral or asymmetric carbon.** The carbon which is bonded to four different atoms or groups of atoms.
- **Enantiomers.** Optical isomers which are non-superimposable mirror images of each other.
- **Diastereomers.** Stereoisomers which are not mirror images of each other.
- **Racemic mixture.** An equimolar mixture of enantiomers *d*-form and *l*-form.
- **Racemisation.** The process of converting *d*- or *l*-form of an optically active compound into racemic form *dl*.
- **Resolution.** The process of separating a racemic mixture into *d*- or *l*-form enantiomers.
- **Meso-compounds.** The compounds which do not show optical activity in spite of the presence of chiral atom.



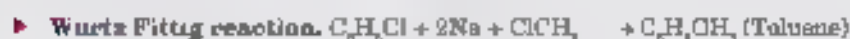
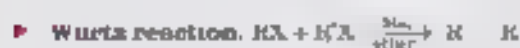
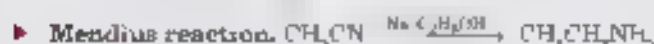
- **Hunsdiecker reaction.** Silver salts of carboxylic acids are decomposed by Br_2 or I_2 .



- **Birnbaum-Simonini reaction.** Iodine forms esters with silver salts.



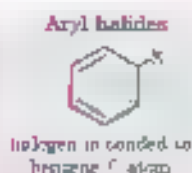
- **Raschig process:**



QUICK CHAPTER ROUND UP

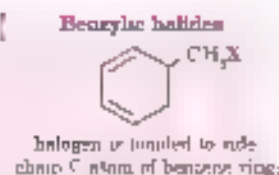
HALOALKANES AND HALOARENES

Alkyl nitrate
 $\text{CH}_3\text{CH}_2\text{X}$
 halogen is bonded to
 alkyl chain



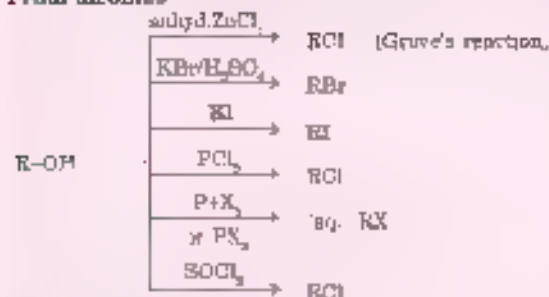
Vinyl: bonded
 $\text{CH}_2=\text{CH}$
 X
 halogens or bonded to a
 double bonded C atom

Allylic halides
 $\text{H}_2\text{C}=\text{CH}-\text{CH}_2-\text{X}$
 halogen is bonded to carbon
 in double bonded C atom

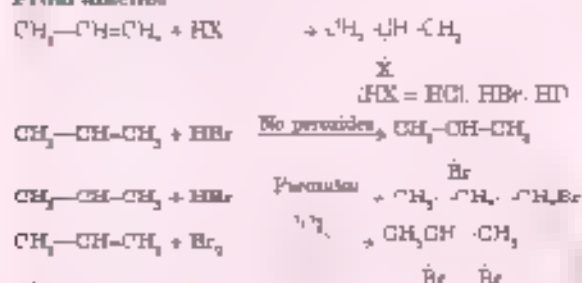


Preparation of Halohalkanes

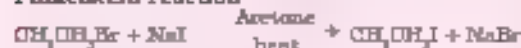
- From alcohol



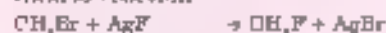
► From Atlanta



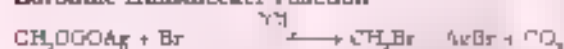
- **Finkelstein reaction**



■ **Нравственная ответственность**

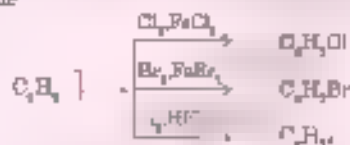


- Barodine Hunsdiecker reaction

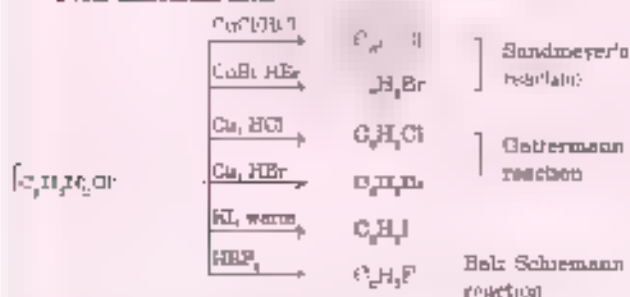


Preparation of Indoleoxide

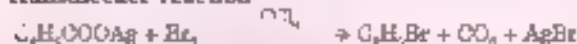
■ From overseas



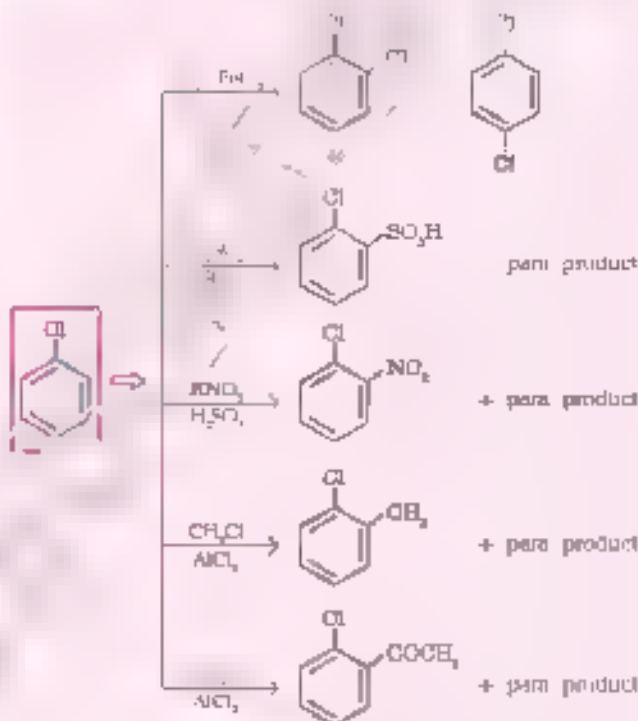
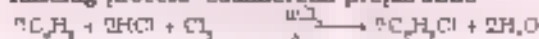
- From diamond sales



- **Hunsdiecker reaction**



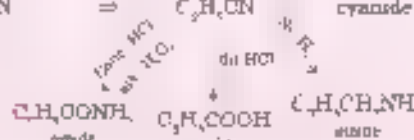
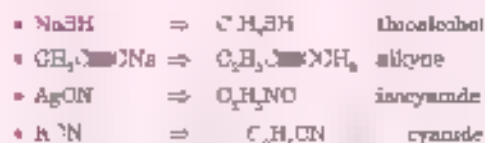
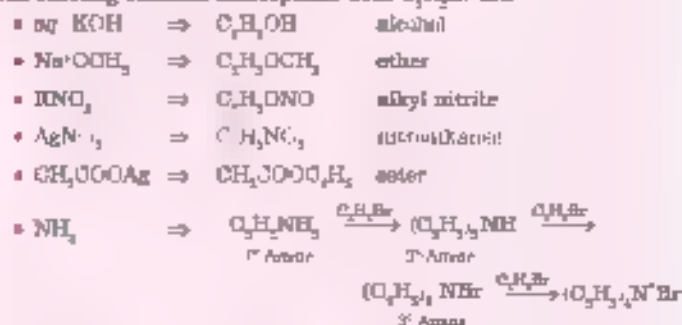
- Raschig process commercial preparation

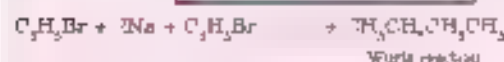
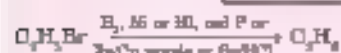
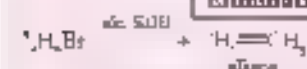


References and Bibliography

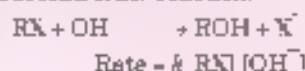
Alkyl halides have polar C-X bonds and undergo nucleophilic substitution reactions.

The reacting common nucleophiles with C_6H_5Br are



Reactions with metals

Reduction

Elimination reactions


The reaction between primary alkyl halide CH_3Br and hydroxide ion OH^- is second order reaction.



In this reaction the nucleophile OH^- attacks the partially positively charged carbon atom of $C-X$ bond from the direction

180° away from the halogen atom. This process occurs in one step.

The reactivity of alkyl halides towards S_N2 mechanism is: methyl $> 1^\circ > 2^\circ > 3^\circ$

The S_N2 reaction is accompanied by inversion of configuration.

The reaction between tertiary alkyl halide $((CH_3)_3CBr)$ and hydroxide ion to form *tert*-butyl alcohol follows first order kinetics. Rate = $k[(CH_3)_3CBr]$ or in general, Rate = $k[RX]$

The S_N1 mechanism occurs through the formation of carbocation.

The order of reactivity is $3^\circ > 2^\circ > 1^\circ > \text{methyl}$

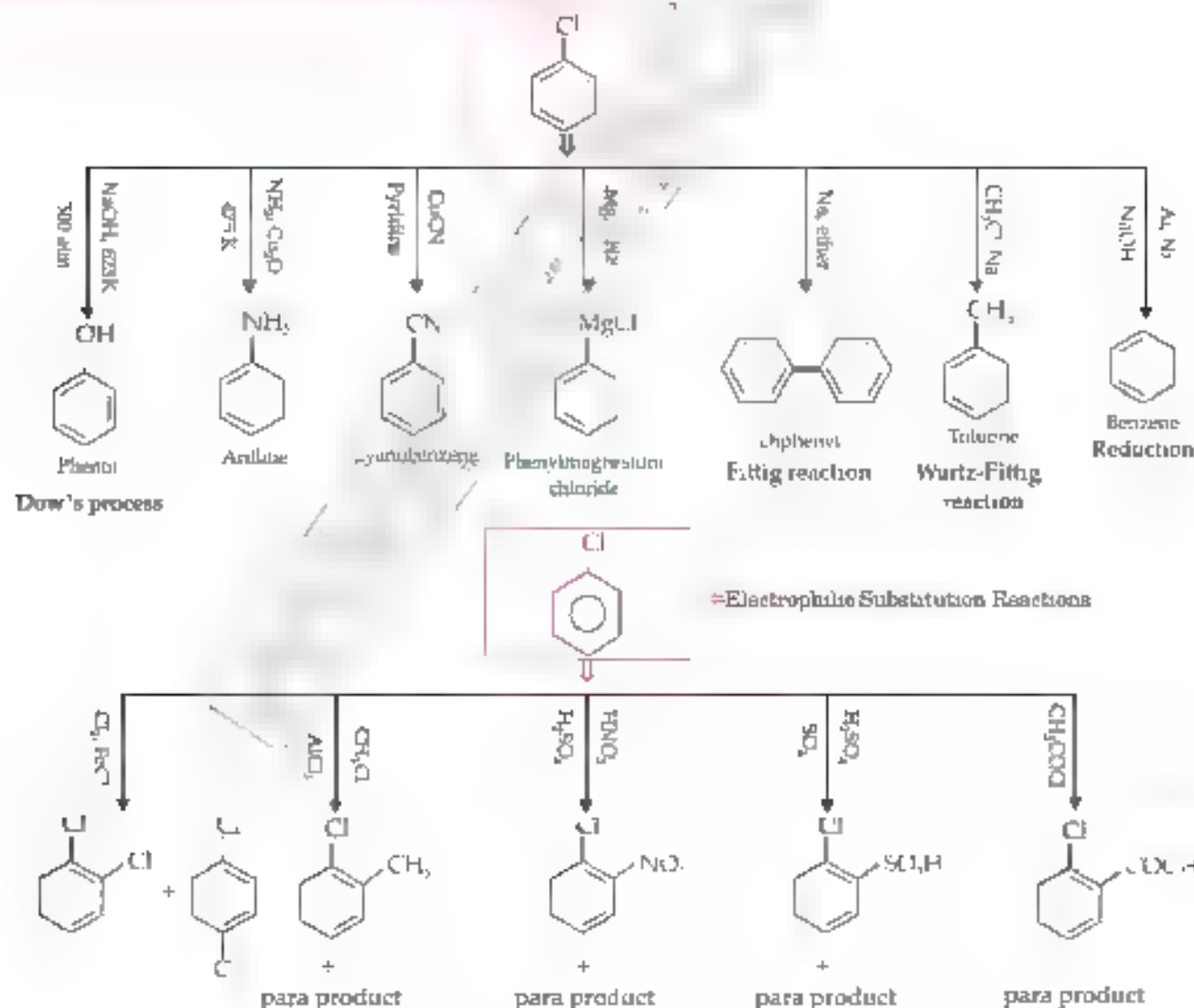
In case of optically active alkyl halides, the product formed is a racemic mixture.

Reactivity of S_N1 vs S_N2

	S_N2 mechanism	S_N1 mechanism
1° alkyl halide	fast	slow
2° alkyl halide	medium	medium
3° alkyl halide	slow	fast

Reactions of Haloarenes

Aryl halides are less reactive than haloalkanes





NCERT FILE

Solved


NCERT
In-text Questions

Q.1. Write the structures of the following compounds :

- 2-Chloro-3-methylpentane
- 1-Chloro-4-ethylcyclohexane
- 4-*tert*-Butyl-3-iodoheptane
- 1,4-Dibromobut-2-ene
- 1-Bromo-4-*sec*-butyl-2-methylbenzene

Ans. Refer Solved Example 3 (Page 11).

Q.3. Why is sulphuric acid not used during the reaction of alcohols with KI ?

Ans. Sulphuric acid is an oxidising agent. It will oxidise HI produced during the reaction to I₂ and therefore will prevent the reaction between an alcohol and HI to form alkyl iodide.

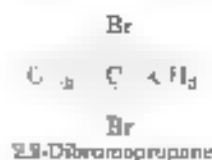
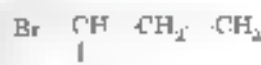


Therefore, a non-oxidising acid such as H₃PO₄ is used instead of H₂SO₄.



Q.3. Write structures of different dihalogen derivatives of propane.

Ans. Four isomeric dihalogen derivatives of propane are formed. For example



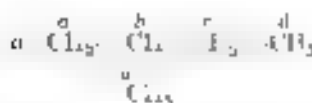
Similarly we may write four dihalogen derivatives of other alkanes.

Q.4. Among the isomeric alkanes of molecular formula C₄H₁₀, identify the one that on photochemical chlorination yields

- A single monochloride
- Three isomeric monochlorides
- Four isomeric monochlorides.

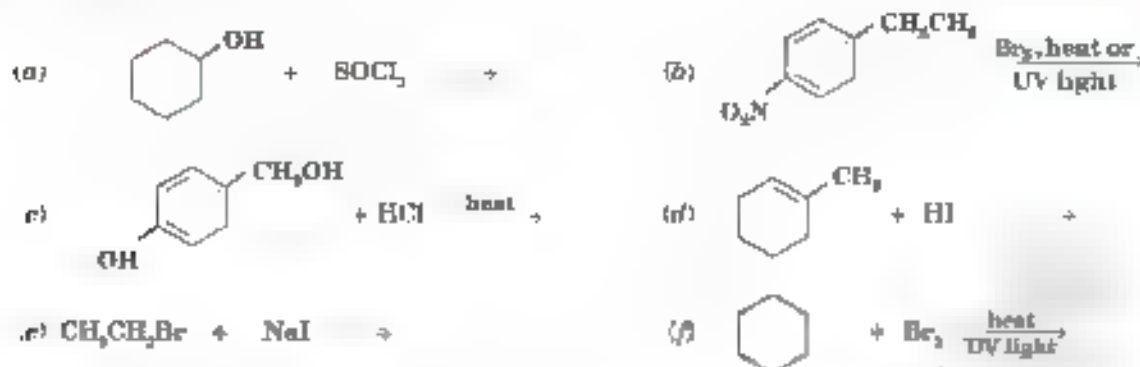


Replacement of a, b or c H atom give different products



Replacement of a, b, c and d H atoms give different products.

Q.5. Draw the structure of major monohalo products in each of the following reactions



Ans. Refer Solved Example 7 (Page 23).

Q.6. Arrange each set of compounds in order of increasing boiling points

(a) Bromomethane, Bromoform, Chloromethane, Dibromomethane

(b) 1-Chloropropane, Isopropyl chloride, 1-Chlorobutane

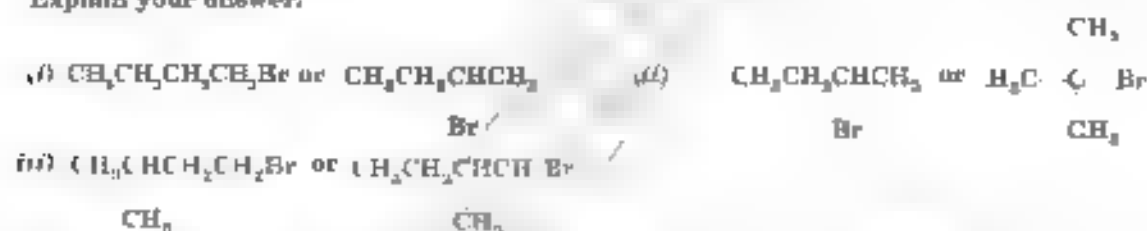
Ans. a For the same alkyl group boiling point increases with the increase in size of the halogen atom. Therefore boiling point of bromomethane is more than that of chloromethane. Further the boiling point increases with increase in number of halogen atoms. Therefore, boiling point of bromoform is higher than that of dibromomethane which is higher than that of bromomethane. Thus, the boiling point increases as



b For the same halogen, boiling point increases with increase in size of the alkyl group due to increase in van der Waals forces of attraction. Therefore boiling point of 1-chlorobutane is more than that of 1-chloropropane. Further the boiling point decreases as branching increases so that the boiling point of 1-chloropropane is higher than that of isopropyl chloride. Thus, the boiling point increases as



Q.7. Which alkyl halide from the following pairs would you expect to react more rapidly by an $\text{S}_{\text{N}}2$ mechanism? Explain your answer.



Ans. (i) $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{Br}$ reacts faster than $\text{CH}_3\text{CH}_2\text{CH}(\text{Br})\text{CH}_3$. This is because $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{Br}$ is a 1° alkyl halide while

$\text{CH}_3\text{CH}_2\text{CH}(\text{Br})\text{CH}_3$ is a 2° alkyl halide. Since there will be some steric hindrance in 2° alkyl halide than in 1° alkyl

halide, it will react slowly.

(ii) $\text{CH}_3\text{CH}_2\text{CH}(\text{Br})\text{CH}_3$ will react faster than $\text{H}_3\text{C}-\text{C}(\text{Br})(\text{CH}_3)_2$ as there will be lesser steric hindrance in 2° alkyl halide as compared to

3° alkyl halide.

(iii) $\text{CH}_3\text{CH}(\text{CH}_3)\text{CH}_2\text{CH}_2\text{Br}$ and $\text{CH}_3\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{Br}$ are 1° alkyl halides. But in II the CH_3 group is at α atom

which is closer to Br atom while in I the CH_3 group is at β atom, which is away from Br atom. Therefore, alkyl

halide II has greater steric hindrance than I. Thus $\text{CH}_3\text{CH}(\text{CH}_3)\text{CH}_2\text{CH}_2\text{Br}$ reacts faster than $\text{CH}_3\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{Br}$.

Q.8. In the following pairs of halogen compounds, which compound undergoes faster S_N1 reaction?



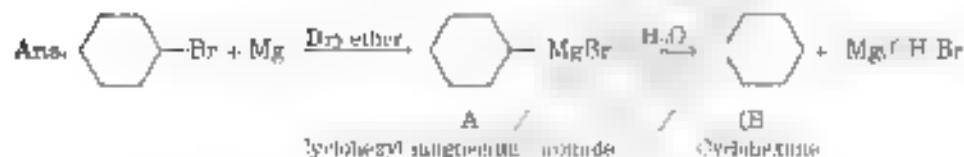
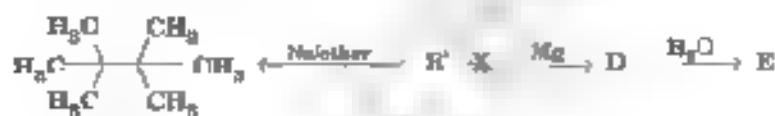
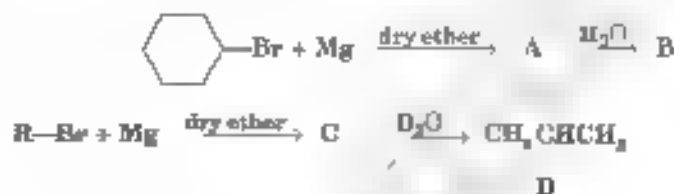
Ans. The reactivity of alkyl halide towards S_N1 reaction depends upon the stability of the intermediate carbocation formed as $3^\circ > 2^\circ > 1^\circ$



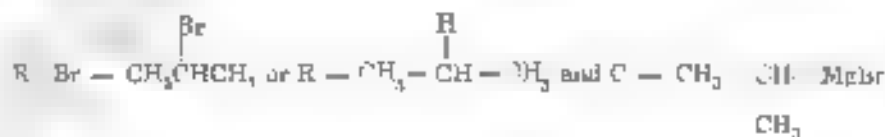
due to the stability of intermediate 3° carbocation,  will react faster



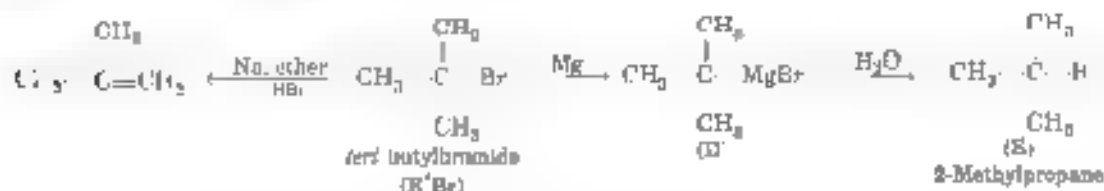
Q.9. Identify A, B, C, D, E, R and R' in the following :



Since D gets attached to same C-atom as which MgBr or Br was present so that



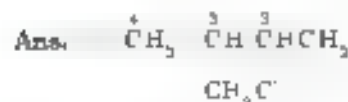
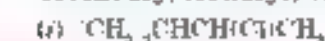
tert-alkyl halides do not undergo Wurtz reaction. Therefore the question is not correct. They undergo dehydrohalogenation to give alkenes. Hence, $\text{R}' = (\text{CH}_3)_2\text{CH}$



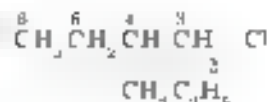


Textbook Exercises

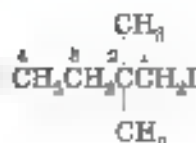
Q.1 Name the following halides according to IUPAC system and classify them as alkyl, aryl, benzyl (primary, secondary, tertiary), vinyl or aryl halides :



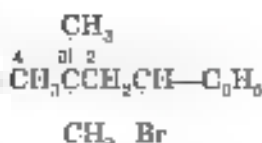
2-Chloro-3-methylbutane : 2°-alkyl halide



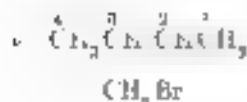
5-Chloro-4-methylhexane : 2°-alkyl halide



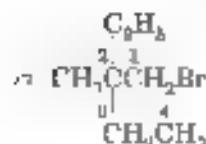
1-Iodo-2, 2-dimethylbutane : 1°-alkyl halide



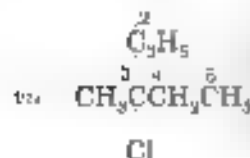
1-Bromo-3, 3-dimethyl-1-phenylbutane : 2°-benzylic halide



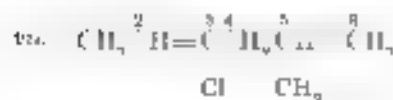
Bromo-3-methylpentane : 3°-alkyl halide



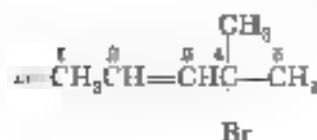
1-Bromo-2-ethyl-2-methylbutane : 1°-alkyl halide



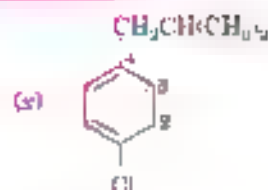
3-Chloro-3-methylpentane : 3°-alkyl halide



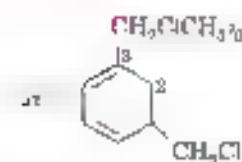
3-Chloro-5-methylhex-2-ene : vinylic halide



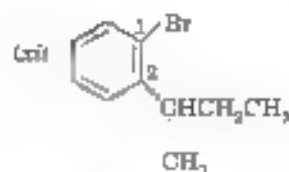
4-Bromo-4-methylpent-2-ene : allylic halide



1-Chloro-4-(2-methylpropyl) benzene (aryl halide)

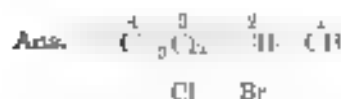


1-Chloro-1-methyl-2-(2,4-dimethylpropyl) benzene (1°-benzyl halide)

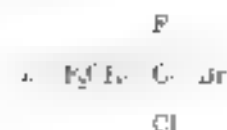


1-Bromo-2-(1-methylpropyl) benzene (aryl halide)

Q.2. Give the IUPAC names of the following compounds



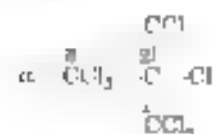
2-Bromo-3-chlorobutane



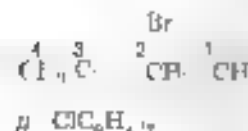
1-Bromo-1-chloro-1,2,2-trifluoroethane



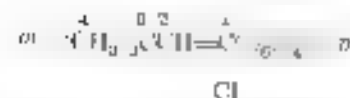
1-Bromo-4-chlorobut-2-yne



2-(Trichloromethyl)-1,1,1,2,3,3,3-heptachloropropane



2-Bromo-3,3-bis(4-chlorophenyl)butane

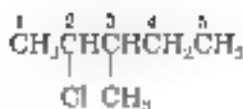


1-Chloro-1-(4-iodophenyl)-3,5-dimethylbut-1-ene

Q.3. Write the structure of the following organic halogen compounds



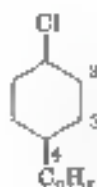
Ans. 2-Chloro-3-methylpentane



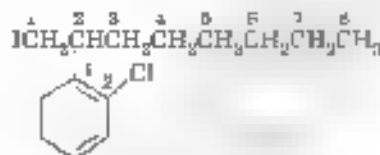
(i) *p*-Bromochlorobenzene



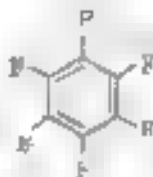
(ii) 1-Chloro-4-ethylcyclohexane



(iii) 2-(1-chlorophenyl)-1-octadecane



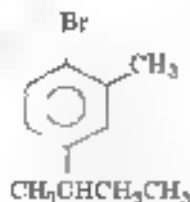
(iv) Perfluorobenzene



(v) 4-tert-Butyl-3-iodoheptane



(vi) 1-Bromo-4-sec-butyl-2-methyl benzene



(vii) 1,4-Dibromobut-2-ene



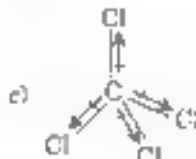
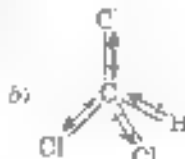
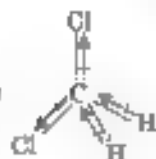
Q.4. Which one of the following has highest dipole moment ?

(a) CH_2Cl_2

(b) CHCl_3

(c) CCl_4

Ans. (a)

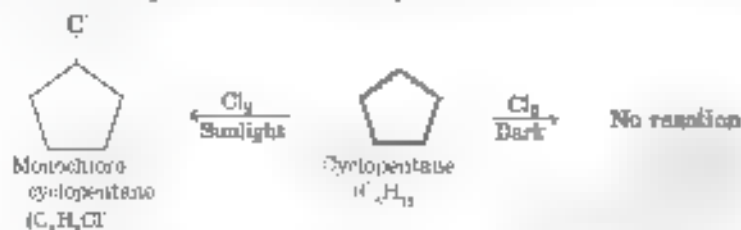


CCl_4 is symmetrical and has resultant zero dipole moment. In CHCl_3 , the resultant of two $\text{C}-\text{Cl}$ dipoles is opposed by resultant of $\text{C}-\text{H}$ and $\text{C}-\text{H}$ bonds. Since the latter resultant is expected to be smaller than the former, CHCl_3 has a definite dipole moment. It has been found to have dipole moment of 1.08D. In CH_2Cl_2 , the resultant of two $\text{C}-\text{Cl}$ bonds is reinforced by the resultant of two $\text{C}-\text{H}$ dipoles and therefore, it has a higher dipole moment than CHCl_3 . It has been found to have dipole moment of 1.62D.

Thus, CH_2Cl_2 has the highest dipole moment.

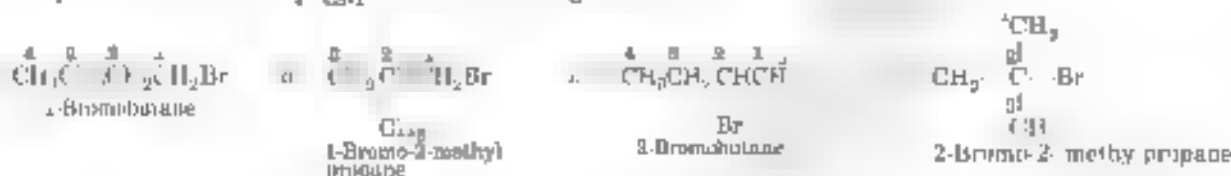
Q.5. A hydrocarbon C_5H_{10} does not react with chlorine in dark but gives a single monochloro compound C_5H_9Cl in bright sunlight. Identify the hydrocarbon.

- Ans.** The molecular formula suggests that it can either be a cycloalkane or alkene. Since the hydrocarbon does not react with Cl_2 in the dark, it cannot be an alkene. Therefore, it must be a cycloalkane.
- i. The hydrocarbon reacts with Cl_2 in the presence of bright sunlight to give a single monochloro compound C_5H_9Cl , therefore, all the ten H-atoms of the cycloalkane must be equivalent.



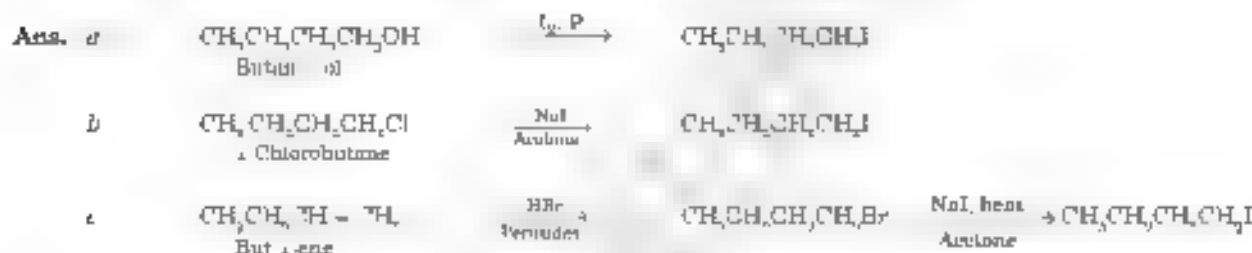
Q.6. Write the isomers of the compound having formula C_4H_9Br .

Ans. The compound is saturated $C_{4+2n-2}H_{9+2n-2}Br$. It has following four isomers



Q.7. Write the equations for the preparation of 1-iodobutane from

- (a) 1-butanol (b) 1-chlorobutane (c) but 1-ene



Q.8. What are ambident nucleophiles? Explain with an example.

Ans. The nucleophiles which can attack through two different sites are called ambident nucleophiles. For example cyanide is an ambident nucleophile because it can attack through C or N because of the following resonance structures



Q.9. Which compound in each of the following pairs will react faster in S_N2 reaction with OH^- ?

- (a) CH_3Br or CH_3I (b) $(CH_3)_3CCl$ or CH_3Cl (D.S.B. 2008)

Ans. a CH_3I reacts faster than CH_3Br in S_N2 reaction with OH^- because I^- ion is a better leaving group than Br^- ion.
 b CH_3Cl is more reactive than $(CH_3)_3CCl$ because of steric hindrance in case of $(CH_3)_3CCl$.

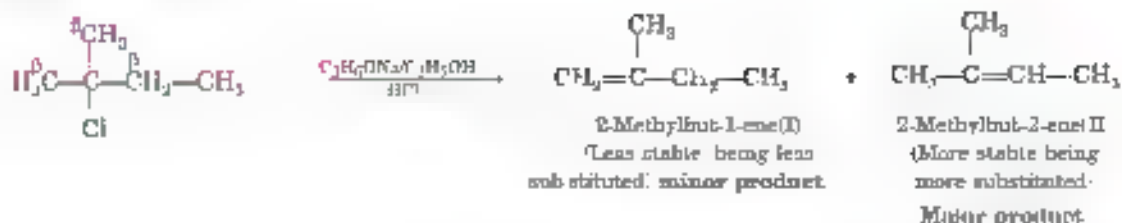
Q.10. Predict all the alkenes that would be formed by dehydrohalogenation of the following halides with sodium ethoxide in ethanol and identify the major alkene.

- (a) 1-Bromo-1-methylcyclohexane (b) 2-Chloro-2-methylbutane
 (c) 2,2,3-Trimethyl-3-bromopentane

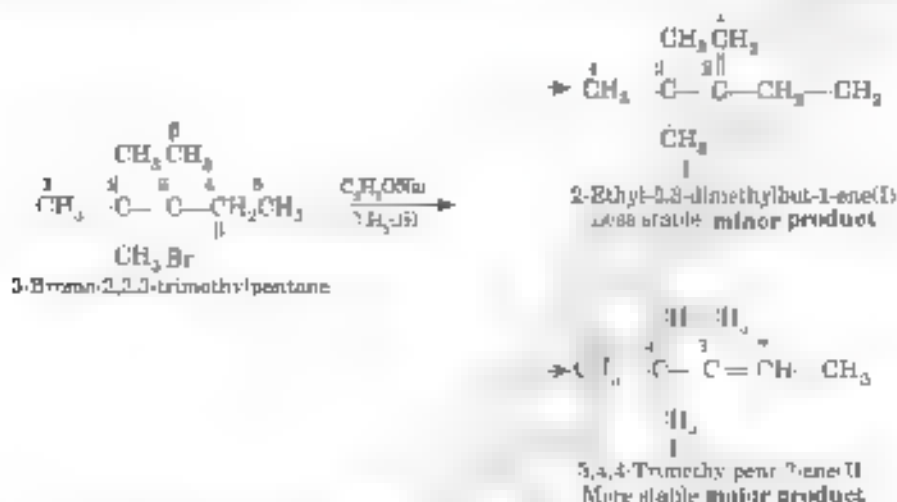
Ans. a In 1-bromo-1-methylcyclohexane, β -hydrogens on either side of the Br atom are equivalent and hence only one alkene is formed



b In 2-chloro-2-methylbutane, there are two different sets of equivalent β -hydrogens and therefore, it can give two alkenes I and II. But according to Saytzeff rule, more highly substituted alkene II being more stable is the major product.



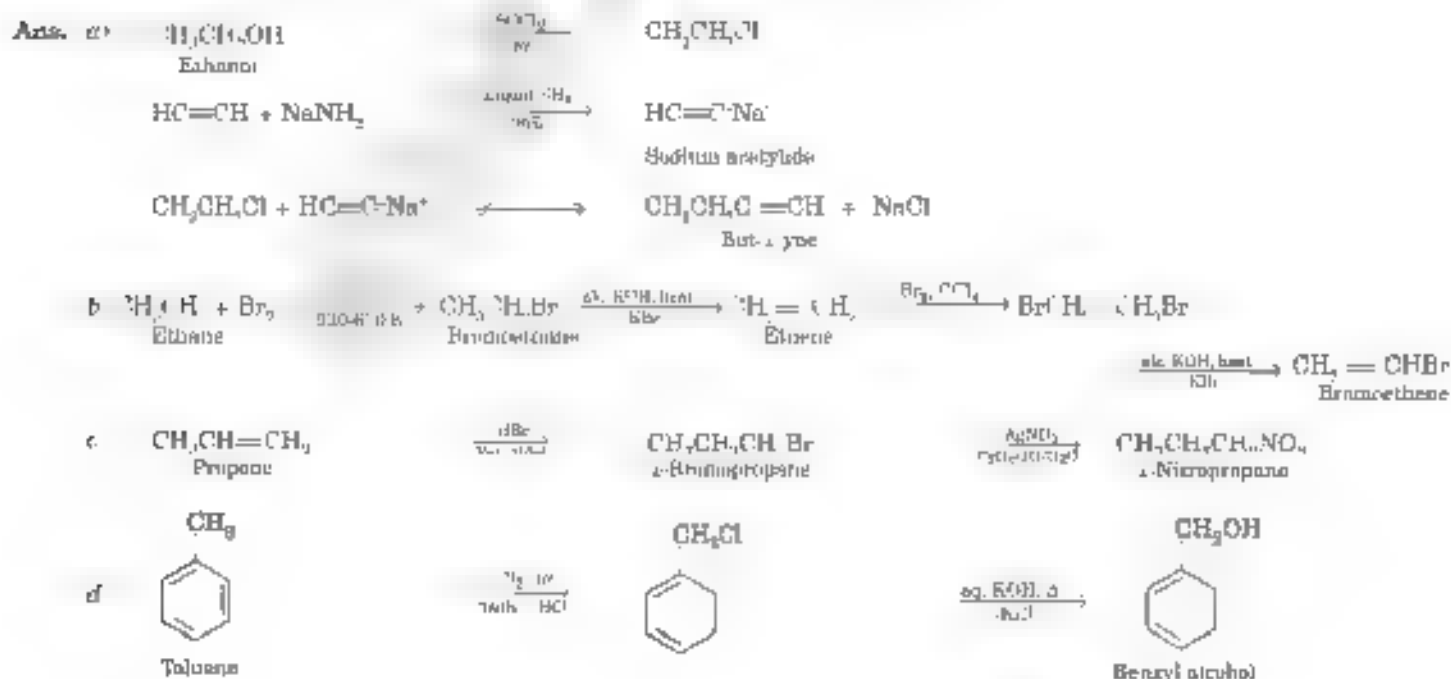
- c. 3-Bromo-2,2,3-trimethylpentane has two different β -hydrogen atoms and hence gives two different alkenes I and II. But according to Saytzeff rule, more highly substituted alkene II being more stable is the major product.

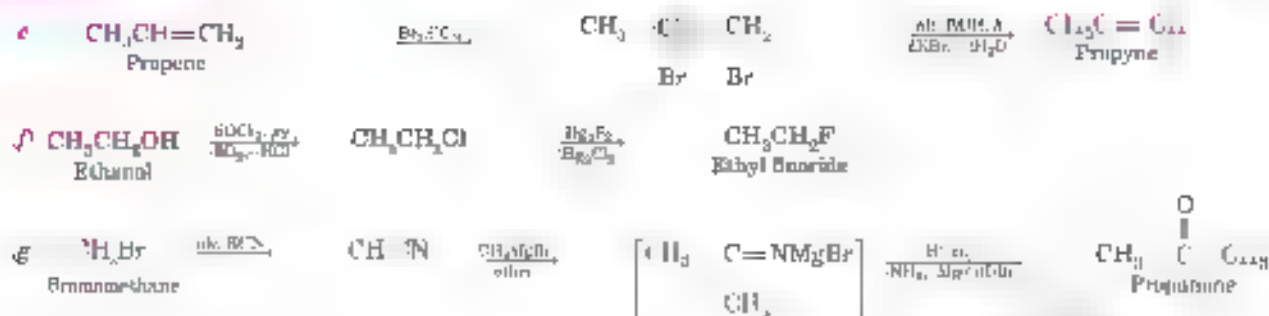


Alkene II is more substituted than alkene I and hence is more stable according to Saytzeff rule.

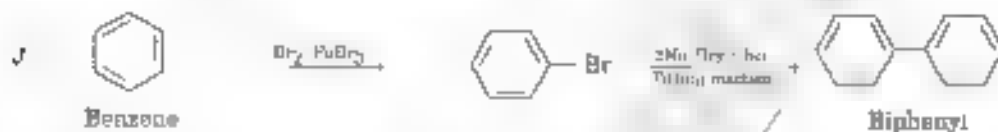
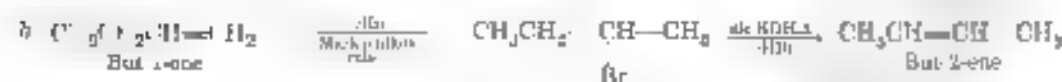
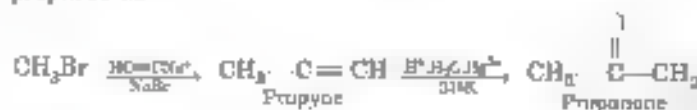
Q.11. How will you bring the following conversions?

- | | |
|--------------------------------|-------------------------------|
| (a) Ethanol to but-1-yne | (b) Ethane to bromoethene |
| (c) Propene to 1-nitropropane | (d) Toluene to benzyl alcohol |
| (e) Propene to propyne | (f) Ethanol to ethyl fluoride |
| (g) Bromomethane to propanone | (h) But-1-ene to but-2-ene |
| (i) 1-Chlorobutane to n-octane | (j) Benzene to biphenyl |





It can also be prepared as



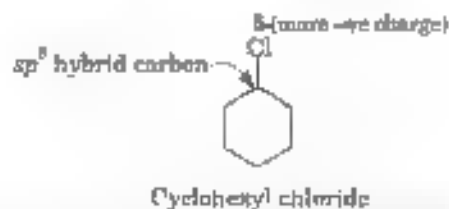
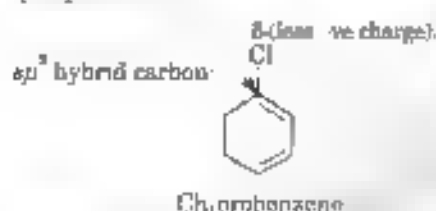
Q.12. Explain why

- the dipole moment of chlorobenzene is lower than that of cyclohexyl chloride.
- alkyl halides, though polar, are immiscible with water.
- Grignard reagents should be prepared under anhydrous conditions?

(D.S.B. 8018)

(CBSE Sample Paper 2011)

Ans. a) In chlorobenzene, the C of C-Cl bond is sp^2 -hybridised while the C of C-Cl bond in cyclohexyl chloride is sp^3 -hybridised.



Therefore, the sp^2 -hybridised carbon of chlorobenzene has more s-character and hence more electronegative than the sp^3 -hybridised carbon of cyclohexyl chloride. As a result, the sp^2 -hybridised carbon of C-Cl bond in chlorobenzene has less tendency to release electrons to Cl than the sp^3 -hybridised carbon of cyclohexyl chloride. As a result, the C-Cl bond in chlorobenzene is less polar than in cyclohexyl chloride. Thus, chlorobenzene is less polar than cyclohexyl chloride.

In other words, the magnitude of negative charge δ^- is less on Cl atom of chlorobenzene than in cyclohexyl chloride. Further, due to delocalisation of lone pair of electrons of the Cl atom over the benzene ring due to resonance, C-Cl bond in chlorobenzene acquires some double bond character. On the other hand, C-Cl bond in cyclohexyl chloride is a pure single bond.



Since dipole moment is a product of charge and distance, therefore chlorobenzene has lower dipole moment than cyclohexyl chloride due to lower magnitude of charge δ^- on Cl atom and small C-Cl distance.

- b) Alkyl halides are polar molecules and therefore, their molecules are held together by dipole-dipole forces. On the other hand, the molecules of H_2O are held together by hydrogen bonds. When alkyl halides are added to water, the new forces of attraction between water and alkyl halide molecules are weaker than the forces of attraction already existing

between alkyl halide-alkyl halide molecules and water-water molecules. Hence alkyl halides are immiscible, not soluble in water.

- c. Grignard reagents are very reactive. They react with the moisture present in the apparatus or the starting materials RX or Mg .



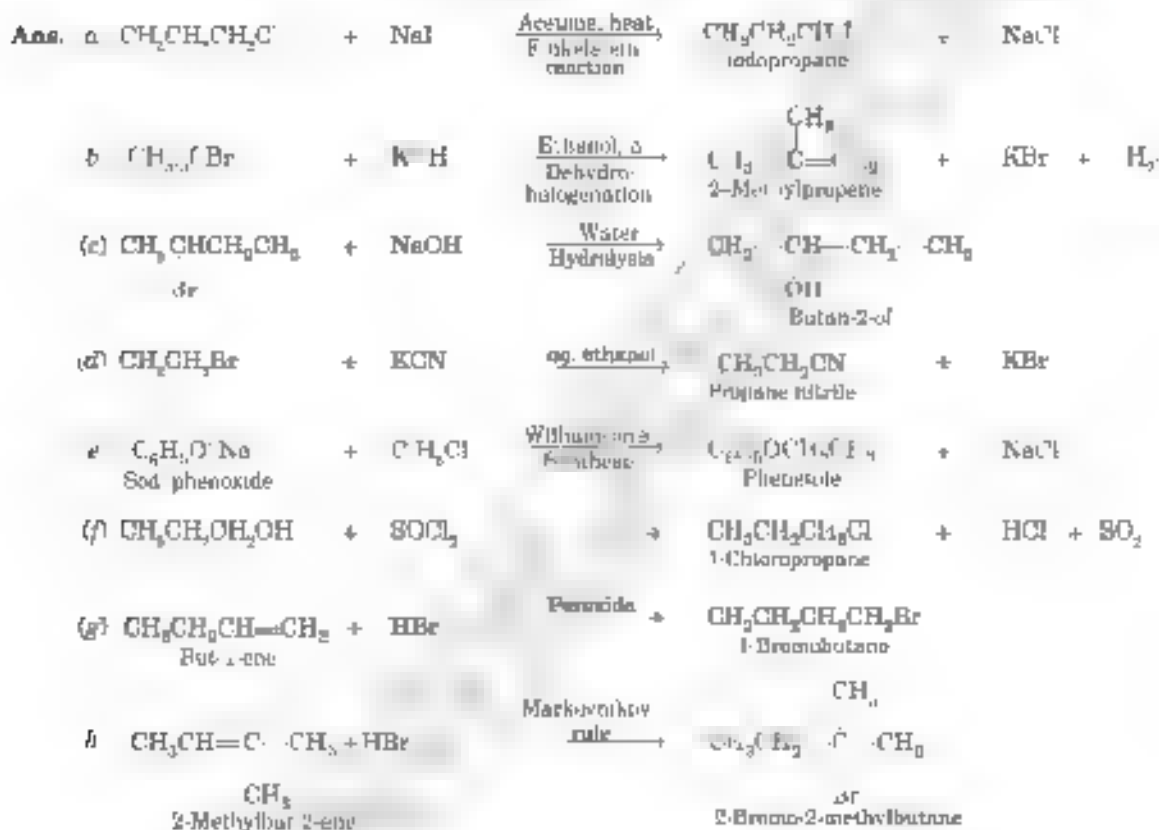
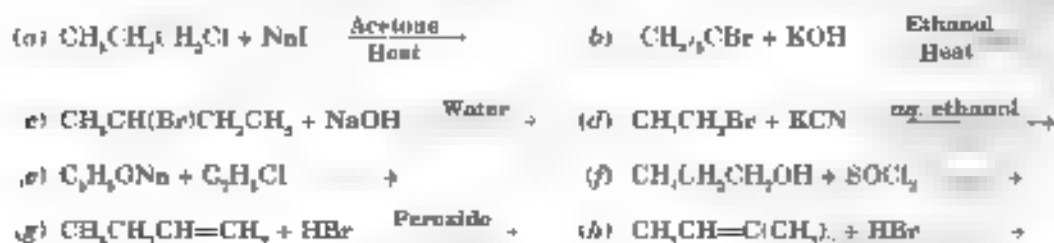
Therefore, Grignard reagents must be prepared in anhydrous conditions.

Q.13. Give the uses of

Freon 12, DDT, carbon tetrachloride and iodoform.

Ans. Refer Text Book for uses of Freon 12 (Page 74), DDT (Page 74-75), Carbon tetrachloride (Page 74), iodoform (Page 74).

Q.14. Write the structure of the major organic product in each of the following reactions



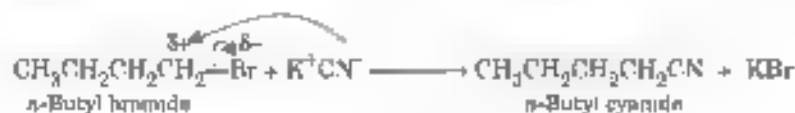
Q.15. Explain the following reaction :



Ans. KCN has nucleophile CN^- ion which is ambident nucleophile because of the following two contributing structures



Therefore, CN^- can attack the carbon atom of $C-Br$ bond of $n\text{-BuBr}$ either through C or N . Since $C-C$ bond is stronger than $C-N$ bond, therefore the attack occurs through C to form n -butyl cyanide as



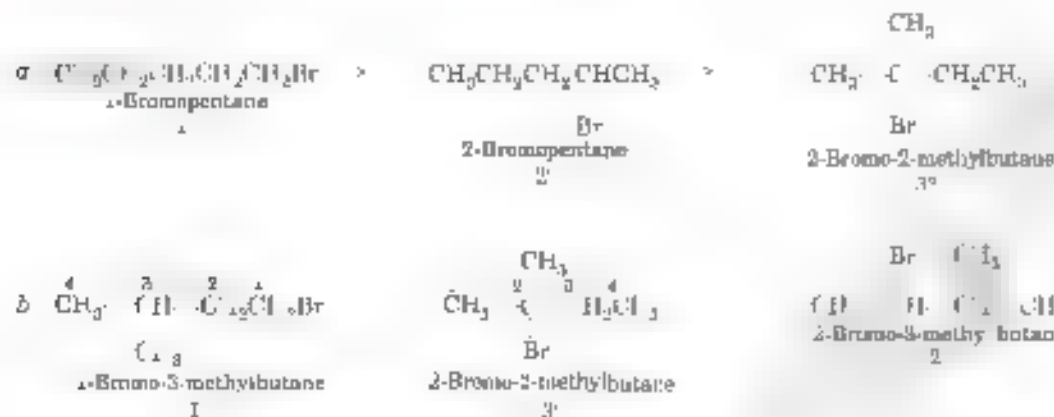
Q.16. Arrange the compounds of each set in order of reactivity towards S_N2 displacement

(a) 2-Bromo-2-methylbutane, 1-Bromopentane, 2-Bromopentane

(b) 1-Bromo-3-methylbutane, 3-Bromo-2-methylbutane, 2-Bromo-2-methylbutane

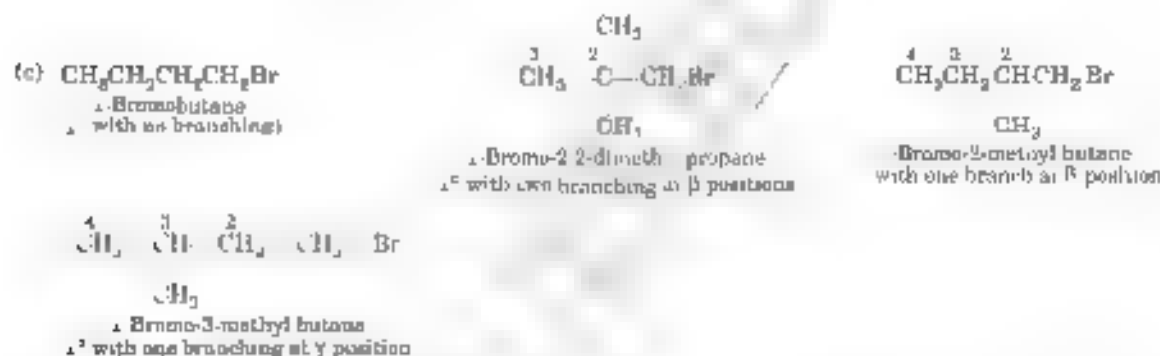
(c) 1-Bromobutane, 1-Bromo-2,2-dimethylpropane, 1-Bromo-2-methylbutane, 1-Bromo-3-methylbutane

Ans. The reactivity in S_N2 reaction depends upon steric hindrance. Lesser the steric hindrance more the reactivity. Therefore, the reactivity of different alkyl halides towards S_N2 reactions is $1^\circ > 2^\circ > 3^\circ$



So, the order of reactivity is

1-Bromo-3-methylbutane > 2-Bromo-3-methylbutane > 3-Bromo-2-methylbutane

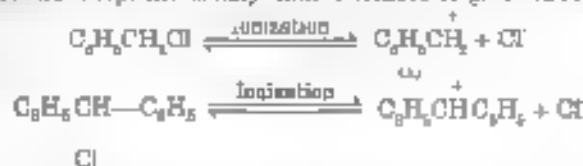


Thus, reactivity decreases with steric hindrance as

1-Bromobutane > 1-Bromo-3-methylbutane > 1-Bromo-2-methylbutane > 1-Bromo-2,2-dimethylpropane

Q.17. Out of $\text{C}_6\text{H}_5\text{CH}_2\text{Cl}$ and $\text{C}_6\text{H}_5\text{CHClC}_6\text{H}_5$ which is more easily hydrolysed by aqueous KOH?

Ans. $\text{C}_6\text{H}_5\text{CH}_2\text{Cl}$ is a 1° alkyl halide and $\text{C}_6\text{H}_5\text{CHClC}_6\text{H}_5$ is a 2° alkyl halide. In S_N1 reaction, the reaction proceeds through the formation of carbocation. In the first step, the alkyl halide ionizes to give carbocation



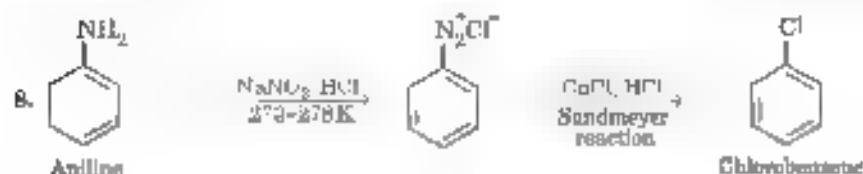
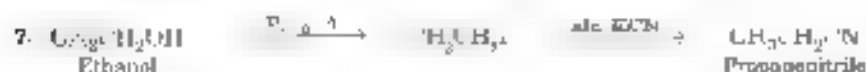
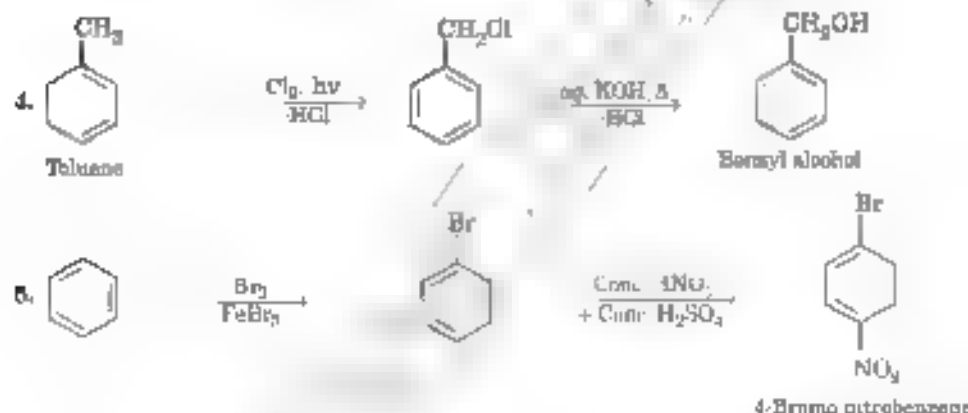
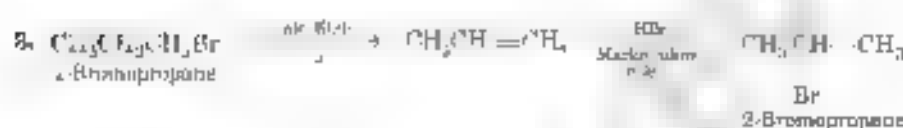
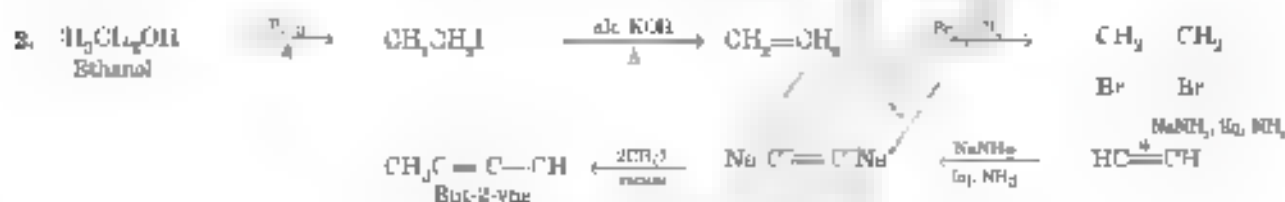
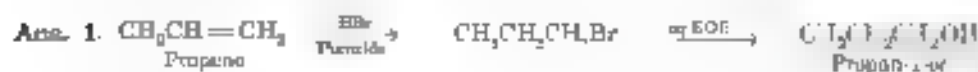
The carbocation II is more stable than I because the +ve charge on carbon can be delocalised over two benzene rings. On the other hand, the +ve charge on carbocation I is delocalised over only one benzene ring. Therefore, $\text{C}_6\text{H}_5\text{CH}_2\text{Cl}$ can be more easily hydrolysed via S_N1 reaction. However, in S_N2 reactions, the reactivity depends upon the steric hindrance. Therefore, $\text{C}_6\text{H}_5\text{CH}_2\text{Cl}$ will get hydrolysed more easily than $\text{C}_6\text{H}_5\text{CHClC}_6\text{H}_5$ because of less steric hindrance.

Q.18. *p*-Dichlorobenzene has higher m.p. and solubility than those of *o*- and *m*-isomers. Discuss.

Ans. The melting point of *p*-isomer of dichlorobenzene is higher than that of *o*- and *m*-isomers. This is because *p*-isomer has symmetrical structure and therefore, its molecules can easily pack closely in crystal lattice. Hence, it has stronger intermolecular forces of attraction than *o*- and *m*-isomer. Therefore, greater energy is required to break the intermolecular forces to melt or dissolve the *p*-isomer than the corresponding *o*- and *m*-isomers. In other words, the melting point of *p*-isomer is higher and its solubility is lower than the corresponding *o*- and *m*-isomers.

Q.19. How the following conversions can be carried out *

- Propene to propan-1-ol
- 1-Bromopropane to 2-bromopropane
- Benzene to 4-bromonitrobenzene
- Ethanol to propanenitrile
- 2-Chlorobutane to 3,4-dimethylhexane
- Ethyl chloride to propanoic acid
- 2-Chloropropane to 1-propanol
- Chlorobenzene to *p*-nitrophenol
- Chloroethane to butane
- tert*-Butyl bromide to isobutylbromide
- Ethanol to but-2-yne
- Toluene to benzyl alcohol
- Benzyl alcohol to 2-phenylethanoic acid
- Aniline to chlorobenzene
- 2-Methyl-1-propene to 2-chloro-2-methylpropane
- But-2-ene to *n*-butyl iodide
- Isopropylalcohol to iodoform
- 2-Bromopropane to 1-bromopropane
- Benzene to diphenyl
- Aniline to phenylisocyanide



9. $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3 \xrightarrow[\text{Wurtz reaction}]{\text{Na}}$ $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{CH}_3$
 2-Chlorobutane 3,4-Dimethylhexane
10. $\text{CH}_3\text{C}(\text{CH}_3)=\text{CH}_2 \xrightarrow[\text{Markovnikov addition}]{\text{HCl}}$ $\text{CH}_3\text{C}(\text{CH}_3)(\text{H})\text{CH}_2\text{Cl}$
 2-Methylpropene 2-Chloro-2-methylpropane
11. $\text{CH}_3\text{CH}_2\text{CH}_2\text{Cl} \xrightarrow{\text{alc. KCN}} \text{CH}_3\text{CH}_2\text{CH}_2\text{CN} \xrightarrow[\text{Hydrolysis}]{\text{H}_2\text{O}}$ $\text{CH}_3\text{CH}_2\text{CH}_2\text{COOH}$
 Ethyl chloride Propanoic acid
12. $\text{CH}_3\text{CH}_2\text{CH}=\text{CH}_2 \xrightarrow[\text{Peroxide}]{\text{HBr}}$ $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{Br} \xrightarrow[\text{Arylation}]{\text{NaI}}$ $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{I}$
 But-1-ene n-Butyl iodide
13. $\text{CH}_3\text{CHClCH}_3 \xrightarrow[\Delta]{\text{alc. KOH}}$ $\text{CH}_3\text{CH}=\text{CH}_2 \xrightarrow[\text{Peroxide}]{\text{HBr}}$ $\text{CH}_3\text{CH}_2\text{CH}_2\text{Br} \xrightarrow[\Delta]{\text{aq. NaOH}}$ $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$
 2-Chloropropane Propan-1-ol
14. $\text{CH}_3\text{CH}(\text{OH})\text{CH}_3 + 3\text{I}_2 + 6\text{NaOH} \xrightarrow{\text{Heat}} 3\text{HI} + \text{CH}_3\text{COONa} + 3\text{NaI} + 5\text{H}_2\text{O}$
 Isopropyl alcohol
15. $\text{C}_6\text{H}_5\text{Cl} \xrightarrow[\text{+ Conc. H}_2\text{SO}_4]{\text{Conc. HNO}_3}$ $\text{C}_6\text{H}_4(\text{Cl})(\text{NO}_2) \xrightarrow[\text{+ 400K, dil. HCl}]{\text{aq. NaOH (20\%)}}$ $\text{C}_6\text{H}_4(\text{OH})(\text{NO}_2)$
 Chlorobenzene p-nitrophenol
16. $\text{CH}_3\text{CH}(\text{Br})\text{CH}_3 \xrightarrow[\Delta]{\text{alc. KOH}}$ $\text{CH}_3\text{CH}=\text{CH}_2 \xrightarrow[\text{Peroxide}]{\text{HBr}}$ $\text{CH}_3\text{CH}_2\text{CH}_2\text{Br}$
 2-Bromopropane 1-Bromopropane
17. $\text{CH}_3\text{CH}_2\text{CH}_2\text{Cl} \xrightarrow[\text{reflux}]{\text{Na}}$ $\text{C}_{10}\text{H}_{18}$
 Chloroethane Buzene
18. $\text{C}_6\text{H}_6 \xrightarrow{\text{Br}_2/\text{FeBr}_3}$ $\text{C}_6\text{H}_5\text{Br} \xrightarrow[\text{Fittig reaction}]{\text{Na dry ether}}$ $\text{C}_{12}\text{H}_{10}$
 Benzene Biphenyl
19. $(\text{CH}_3)_3\text{CBr} \xrightarrow[\Delta]{\text{alc. KOH}}$ $(\text{CH}_3)_2\text{C}=\text{CH}_2 \xrightarrow[\text{Peroxide}]{\text{HBr}}$ $(\text{CH}_3)_2\text{CHCH}_2\text{Br}$
 tert-Butyl bromide 2-Methylpropene tert-Butyl bromide
20. $\text{C}_6\text{H}_5\text{NH}_2 + \text{CHCl}_3 + 3\text{NaOH} \xrightarrow[\text{alc.}]{\text{Warm}}$ $\text{C}_6\text{H}_5\text{NC} + 3\text{KCl} + 3\text{H}_2\text{O}$
 Phenylamine Phenylisocyanide

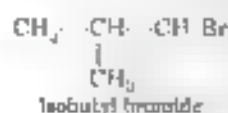
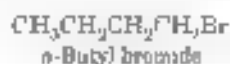
Q.20. The treatment of alkyl chlorides with aqueous KOH leads to the formation of alcohols but in presence of alcoholic KOH, alkenes are major products. Explain.

Ans. In aqueous KOH KOH is almost completely ionized to give OH^- ions. These being strong nucleophiles result into substitution reaction on alkyl chlorides to form alcohols. Moreover in aqueous solution the OH^- ions are highly hydrated/solvated. The hydration reduces the basic character of OH^- ions which therefore, fails to abstract a hydrogen from the β -carbon of the alkyl chloride to form an alkene.

On the other hand, an alcoholic solution of KOH contains alkoxide RO^- ions which being stronger base than OH^- ions preferentially eliminates a molecule of HCl from an alkyl chloride to form alkenes.

Q.21. Primary alkyl halide (a) $\text{C}_4\text{H}_9\text{Br}$ reacted with alcoholic KOH to give compound (b). Compound (b) is reacted with HBr to give (c) which is an isomer of (a). When (a) was reacted with sodium metal it gave a compound (d) C_8H_{18} that was different than the compound when n-butyl bromide was reacted with sodium. Give the structural formula of (a) and write the equations for all the reactions.

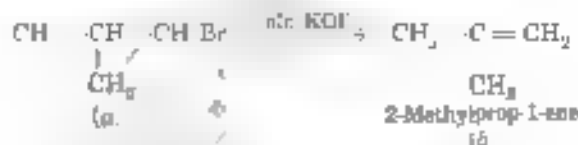
Ans. i) Two primary alkyl halides having the molecular formula $\text{C}_4\text{H}_9\text{Br}$ are possible. These are given below



ii) When compound (a) was reacted with Na metal, it gave a compound (d) C_8H_{18} which was different from the compound obtained when n-butyl bromide was reacted with Na metal and hence the compound (a) must be isobutyl bromide and compound (d) must be 2,5-dimethylhexane



iii) If compound (a) is isobutyl bromide then compound (b) obtained on treatment with alc. KOH must be 2-methylprop-1-ene



iv) Compound (b) on treatment with HBr gives compound (c) in accordance with Markovnikov's rule



(c) is an isomer of compound (a).

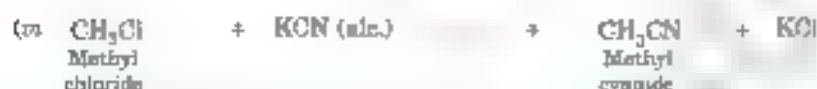
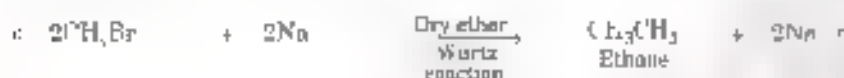
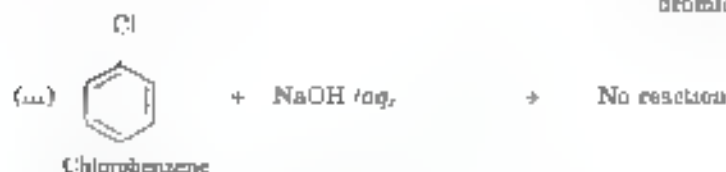
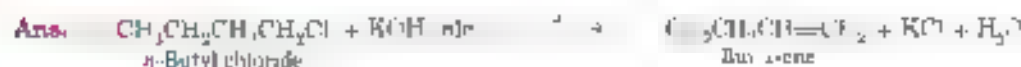
Thus (a) = isobutyl bromide, (b) = 2-Methylprop-1-ene

(c) = tert-Butyl bromide (d) = 2,5-Dimethylhexane

Q.22. What happens when

- n-butyl chloride is treated with alcoholic KOH,
- bromobenzene is treated with Mg in the presence of dry ether,
- chlorobenzene is subjected to hydrolysis,
- ethyl chloride is treated with (aq.) KOH,

- (v) methyl bromide is treated with sodium in the presence of dry ether,
 (vi) methyl chloride is treated with KCN ?



NCERT

Exemplar Problems

Subjective Questions

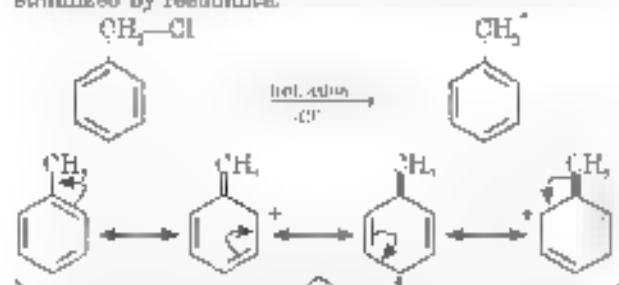
It is due to symmetry of *p*-isomer which fits in crystal lattice better than the *o*-isomer.

- Q.3. Which of the compounds will react faster in $\text{S}_{\text{N}}1$ reaction with the OH^- ion?



Ans. $\text{C}_6\text{H}_5\text{CH}_2\text{Cl}$

$\text{S}_{\text{N}}1$ reaction proceeds through the formation of carbocation intermediate ($\text{C}_6\text{H}_5\text{CH}_2^+$) readily undergoes ionization to give $\text{C}_6\text{H}_5\text{CH}_2^+$ carbocation which is stabilized by resonance.



Benzyl carbocation stabilized by resonance

On the other hand, $\text{CH}_3\text{CH}_2\text{Cl}$ does not undergo ionization to give CH_3CH_2^+ carbocation. Therefore, $\text{C}_6\text{H}_5\text{CH}_2\text{Cl}$ reacts faster than $\text{CH}_3\text{CH}_2\text{Cl}$ with OH^- ion.

- Q.4. Why has iodoform appreciable antiseptic property?

Ans. Due to liberation of free iodine when it comes in contact with skin.

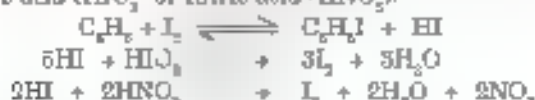
Notes

Objective Questions from Exemplar Problems are given in Competition File, page 144

Short Answer Type Questions

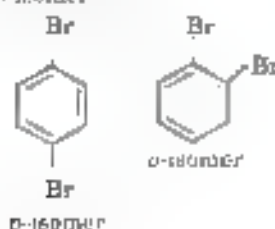
- Q.1. Aryl chlorides and bromides can be easily prepared by electrophilic substitution of arenes with chlorine and bromine respectively in the presence of Lewis acid catalysts. But why does preparation of aryl iodides requires presence of an oxidising agent?

Ans. Iodination reactions are reversible in nature. Therefore, to carry out the reaction in the forward direction, HI formed during iodination is removed by oxidation with iodic acid (HIO_3) or nitric acid (HNO_3).



- Q.2. Out of *o*- and *p*-dibromobenzene which one has higher melting point and why?

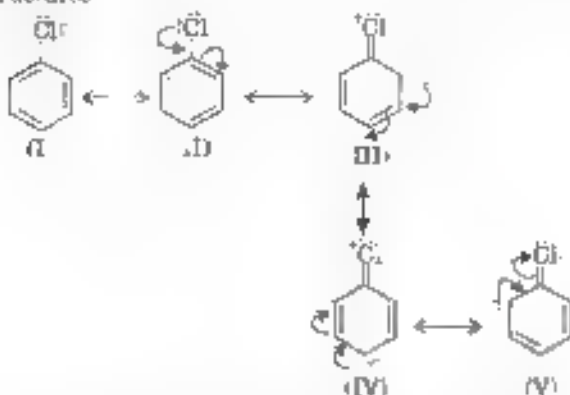
Ans. *p*-Dibromobenzene has higher melting point than its isomer.



Q.5. Haloarenes are less reactive than haloalkanes and haloalkenes. Explain.

Ans. Haloarenes are much less reactive than haloalkanes and haloalkenes towards nucleophilic substitution reactions because of the following reasons

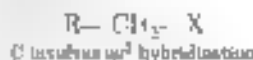
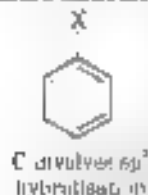
- 1. Resonance effect** In haloarenes there is delocalisation of electrons due to resonance. For example, chlorobenzene is considered to be a resonance hybrid of the following structures



It is evident that the contribution of structures II, IV and V imparts a partial double bond character to the carbon-chlorine bond. This is confirmed by X-ray analysis which shows that the C—Cl bond length in chlorobenzene is 1.69 Å while the C—Cl bond length in ethyl chloride molecule is 1.82 Å. The shortening of bond length imparts stability to aryl halides and the bond cleavage becomes rather difficult. The aryl halides are, therefore, less reactive than alkyl halides.

In haloalkenes also, the filled p -orbital of halogen atom cannot overlap sideways with the unhybridised p -orbital of C atom. Therefore, C—Cl bond is not very strong and can be easily cleaved.

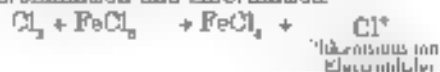
- 2. Different hybridisation states of carbon atom** In haloalkanes the carbon atom of the C—X bond is sp^3 hybridised while in haloarene halides, the carbon atom is sp^2 hybridised. The sp^2 hybridised carbon atom with a greater s -character is more electronegative. It can hold the electron pair of the bond more tightly than the sp^3 hybridised carbon atom in alkyl halides. Therefore, it has less tendency to release electrons to the halogen. As a result, the bond cleavage in aryl halides is somewhat more difficult than in alkyl halides.



Thus haloarenes are less reactive towards the substitution reactions than haloalkanes.

Q.6. Discuss the role of Lewis acids in the preparation of aryl bromides and chlorides in the dark.

Ans. Lewis acids help in generating electrophiles during the bromination and chlorination.

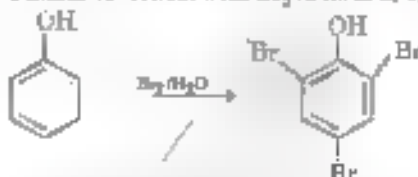


The electrophile then attacks the benzene ring to form a carbocation which loses a proton to form aryl chloride or aryl bromide.

Q.7. Which of the following compounds (a) and (b) will not react with a mixture of NaBr and H_2SO_4 ? Explain why?



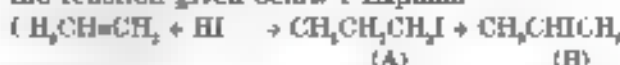
Ans. (b) A mixture of NaBr and H_2SO_4 gives Br_2 gas.
 $2NaBr + 6H_2SO_4 \rightarrow 2NaHSO_4 + 5SO_2 + Br_2 + 2H_2O$
 Phenol (b) reacts with Br_2 to form 2,4,6-tribromophenol.



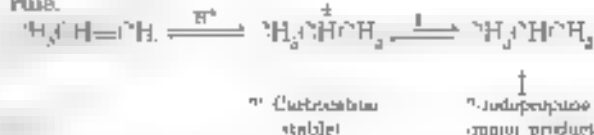
Phenol (b) 2,4,6-tribromophenol

But $CH_3CH_2CH_2OH$ (a) does not react with Br_2 water.

Q.8. Which of the products will be major product in the reaction given below? Explain.



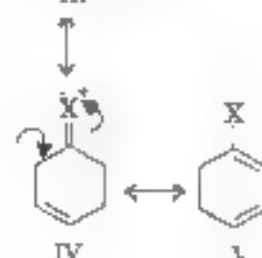
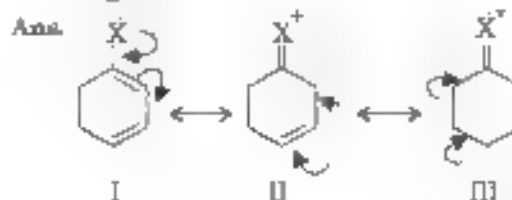
Ans. (B) will be the major product according to Markovnikov's rule.



Q.9. Why is the solubility of haloalkanes in water very low?

Ans. The haloalkanes are only slightly soluble in water. In order to dissolve a haloalkane in water, energy is required to overcome the attractions between the haloalkane molecules and break the hydrogen bonds between water molecules. Since less energy is released in the formation of new attractions between haloalkane and water molecules and these are not very strong as the original hydrogen bonds present in water and hence the solubility of haloalkanes is low.

Q.10. Draw other resonance structures related to the following structure and find out whether the functional group present in the molecule is ortho, para directing or meta directing.



It is clear from resonating structures that there is increase in electron density at ortho and para positions. Therefore the functional group X is ortho and para directing.

Q.11. Classify the following compounds as primary, secondary and tertiary halides.

- (i) 1-Bromobut-2-ene (ii) 4-Bromopent-2-ene
(iii) 2-Bromo-2-methylpropane

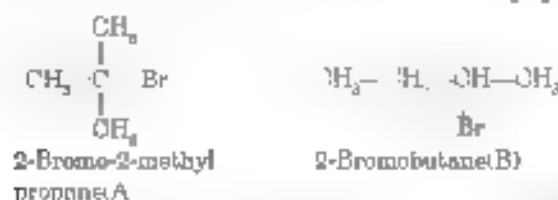
Ans. (i) Primary (ii) secondary (iii) tertiary

Q.12. Compound 'A' with molecular formula C_4H_9Br is treated with aq. KOH solution. The rate of this reaction depends upon the concentration of the compound 'A' only. When another optically active isomer 'B' of this compound was treated with aq. KOH solution, the rate of reaction was found to be dependent on concentration of compound and KOH both.

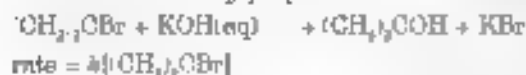
i) Write down the structural formula of both compounds 'A' and 'B'

ii) Out of these two compounds, which one will be converted to the product with inverted configuration.

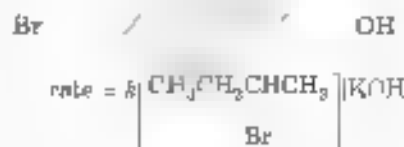
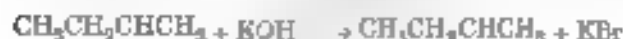
Ans. (i) The molecular formulae of isomers of C_4H_9Br are



Since the rate of reaction of compound 'A' (C_4H_9Br) with aqueous KOH depends upon the concentration of compound 'A' only, therefore, the reaction occurs by S_N1 mechanism and compound A is tertiary bromide i.e. 2-bromo-2-methylpropane



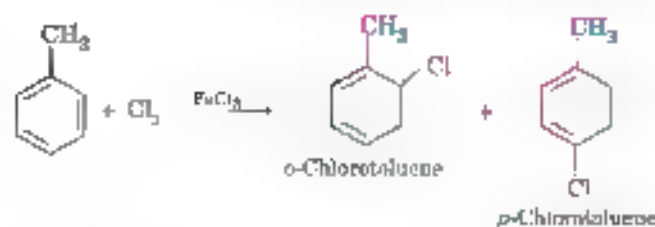
Since compound 'B' is optically active and is an isomer of compound 'A' (C_4H_9Br), therefore, compound 'B' must be 2-bromobutane. Since the rate of reaction of compound 'B' with aqueous KOH depends upon the concentration of compound 'B' and KOH, therefore, the reaction occurs by S_N2 mechanism and product of hydrolysis will have inverted configuration.



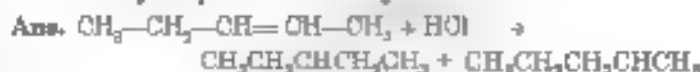
Compound 'B' will be converted with inverted configuration.

Q. 13. Write the structures and names of the compounds formed when compound 'A' with molecular formula, C_7H_8 is treated with Cl_2 in the presence of $FeCl_3$.

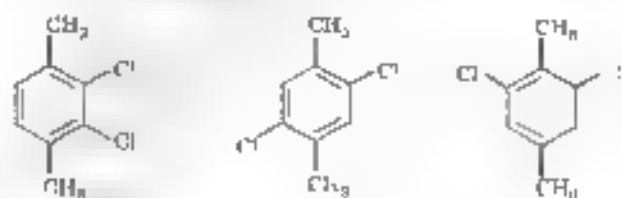
Ans. The compound with molecular formula C_7H_8 is toluene, $C_6H_5CH_3$. Since $-CH_3$ group is o-p-directing, therefore, chlorination of toluene gives o-chlorotoluene and p-chlorotoluene, in which the p-isomer predominates.



Q.14. Identify the products A and B formed in the following reaction



Q. 15. Which of the following compounds will have the highest melting point and why?



Ans. Compound II will have highest melting point. It is because of the symmetry of para positions, thus it fits into crystal lattice better than other isomers.

Q.16. Write down the structure and IUPAC name for neopentyl bromide.

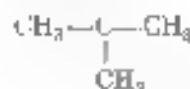


Ans. $CH_3 - C(CH_3)_2 - CH_2Br$ 1-Bromo-2,2-dimethylpropane



Q.17. A hydrocarbon of molecular mass 72 g mol^{-1} gives a single monochloro derivative and two dichloro derivatives on photo chlorination. Give the structure of the hydrocarbon.

Ans. The hydrocarbon having molecular mass 72 g mol^{-1} is C_5H_{12} (pentane). The isomer of pentane which gives single monochloro derivative should have all the 12 hydrogen equivalent. It is



Monochloro derivative $CH_3 - C(CH_3)_2 - CH_2Cl$

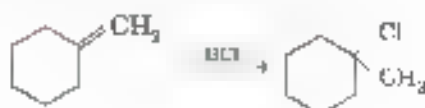


Dichloro derivatives

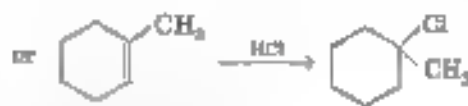


Q.18. Name the alkene which will yield 1-chloro-1-methylcyclohexane by its reaction with HCl. Write the reactions involved.

Ans. Two alkenes are possible. These are methylenecyclohexane and 1-methylenecyclohex-1-ene.



Methylenecyclohexane



1-Methylenecyclohex-1-ene

Q.19. Which of the following haloalkanes reacts with aqueous KOH most easily? Explain giving reason.

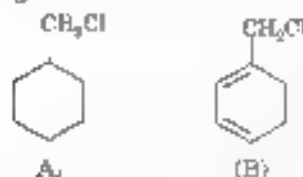
- 1-Bromobutane
- 2-Bromobutane
- 2-Bromo-2-methylpropane
- 2-Chlorobutane

Ans. (iii) 2-Bromo-2-methylpropane (3°) because tertiary carbocation formed during the reaction is most stable.

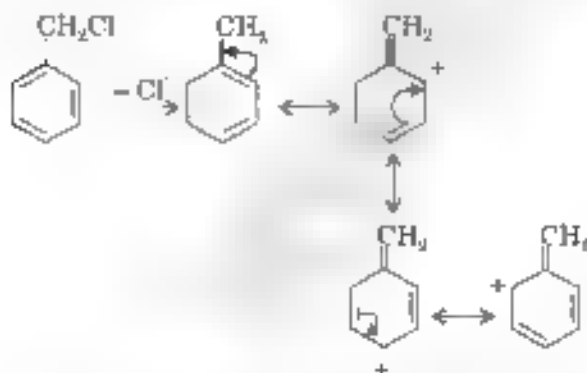
Q.20. Why can aryl halides not be prepared by reaction of phenol with HCl in the presence of ZnCl_2 ?

Ans. This is because C—O bond in phenol is more stable due to resonance effect and it has some double bond character. Therefore, it is difficult to break this bond and hence aryl halides are not prepared by the reaction of phenol with H^+ .

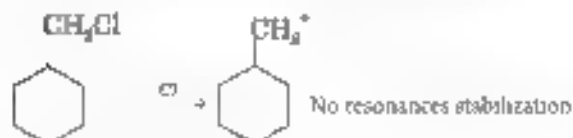
Q.21. Which of the following compounds would undergo $\text{S}_{\text{N}}1$ reaction faster and why?



Ans. (B) Undergoes $\text{S}_{\text{N}}1$ reaction faster because the carbocation formed after the loss of Cl is stabilized by resonance.



On the other hand, the carbocation formed during the reaction of (A) is not resonance stabilized.



Q.22. Allyl chloride is hydrolysed more readily than *n*-propyl chloride. Why?

Ans. Allyl chloride shows high reactivity because the carbocation formed by hydrolysis is stabilised by resonance while no such stabilisation of carbocation exists in the case of *n*-propyl chloride.



Q.23. Why is it necessary to avoid even traces of moisture during the use of a Grignard reagent?

Ans. Grignard reagents are highly reactive and react with water to give corresponding hydrocarbons.



Q.24. How do polar solvents help in the first step in $\text{S}_{\text{N}}1$ mechanism?

Ans. The $\text{S}_{\text{N}}1$ mechanism proceeds through the formation of carbocation. It involves breaking of C—halogen bond for which energy is obtained through the solvation of halide ion with the proton of the protic solvent. Thus polar solvents help in ionisation step by stabilizing the ions by solvation.

Q.25. Write a test to detect the presence of double bond in a molecule.

Ans. The presence of a double bond in a molecule is tested by treating the compound with Br_2 water. The alkenes decolorise the brown colour of Br_2 water.



Q.26. Diphenyls are potential threat to the environment. How are these produced from arylhalides?

Ans. Diphenyls such as *p,p'*-dichlorodiphenyl trichloromethane (DDT) are posing serious environment problems because of its chemical stability and its fat solubility. Its residue accumulates in environment and its long term effects could be highly dangerous.

Diphenyls can be prepared from aryl halides by the following two methods:

Fittig reaction:



(ii) Ullmann biaryl synthesis:



Q.27. What are the IUPAC names of the insecticide DDT and benzenehexachloride?

Why is their use banned in India and other countries?

Ans. DDT 2,4-bis *p*-chlorophenyl-1,1,1-trichloroethane BHC 1,2,3,4,5,6-hexachlorocyclohexane. These have been banned because of their long term toxic effects which could be highly dangerous.

These are non-biodegradable. These insecticides enter the food chains of animals and get deposited in their fatty tissues over a period of time. Therefore, these affect their reproductive system.

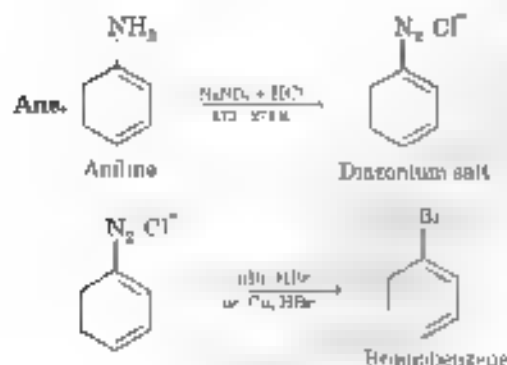
Q.28. Elimination reactions (especially β -elimination) are as common as the nucleophilic substitution reaction in case of alkyl halides. Specify the reagents used in both cases.

Ans. Alkyl halides undergo nucleophilic substitution as well as elimination (β -elimination) reaction.

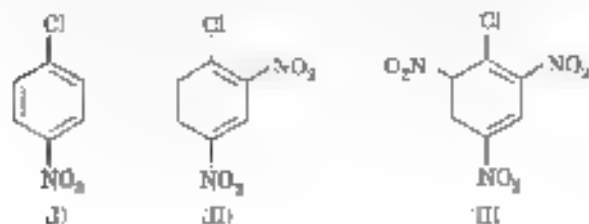
However by proper choice of reagents and reaction conditions, a particular product can be obtained. Usually strong and bulkier bases and high temperature favour elimination reactions while weaker and smaller bases and lower temperature favour substitution reactions. For example, ethyl bromide on heating with alcoholic KOH which contain stronger base $C_2H_5O^-$ ion, at about 473-523 K undergoes elimination to give ethene. But with aqueous KOH at about 373K, it gives ethanol.



Q.29. How will you obtain monobromobenzenes from aniline?



Q.30. Aryl halides are extremely less reactive towards nucleophilic substitution. Predict and explain the order of reactivity of the following compounds towards nucleophilic substitution:

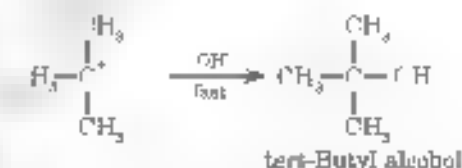
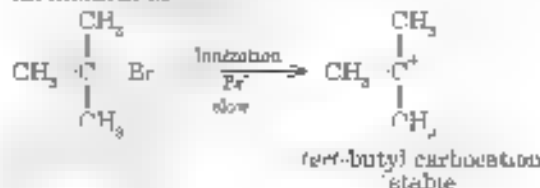


Ans. Presence of electron-withdrawing groups (such as NO_2 at *o*- and *p*- positions with respect to halogen increases the reactivity of halogens towards nucleophilic substitution reactions due to the stability of the intermediate carbanion. More the number of such groups at *o*- and *p*- positions with respect to halogen, higher is the reactivity. Thus the order is III > II > I.

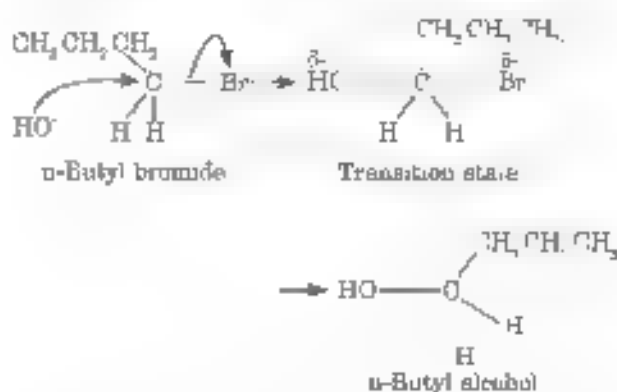
Q.31. *tert*-Butylbromide reacts with aq. NaOH by S_N1 mechanism while *n*-butylbromide reacts by S_N2 mechanism. Why?

Ans. In general, the S_N1 reaction proceeds through the formation of carbocation. The *tert*-butyl bromide readily loses Br^- ion to form stable 3° carbocation.

Therefore, it reacts with aqueous KOH by S_N1 mechanism as



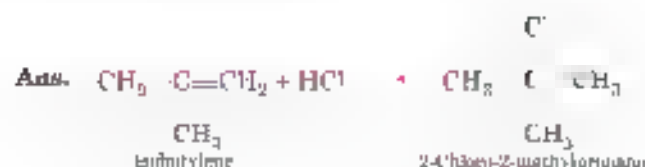
On the other hand, *n*-butyl bromide does not undergo ionization to form *n*-butyl carbocation (1°) because it is not stable. Therefore, it prefers to undergo reaction by S_N2 mechanism, which occurs in one step through a transition state involving nucleophilic attack of OH^- ion from the back side with simultaneous expulsion of Br^- ion from the front side.



S_N1 mechanism follows the reactivity order as $3^\circ > 2^\circ > 1^\circ$ while S_N2 mechanism follows the reactivity order as $1^\circ > 2^\circ > 3^\circ$.

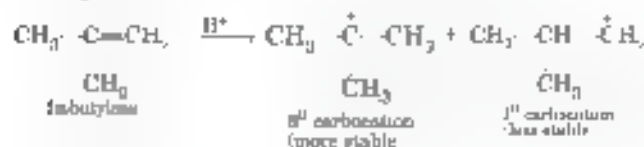
Therefore, *tert*-butylbromide (3°) reacts by S_N1 mechanism while *n*-butylbromide (1°) reacts by S_N2 mechanism.

Q.32. Predict the major product formed when HCl is added to isobutylene. Explain the mechanism involved.

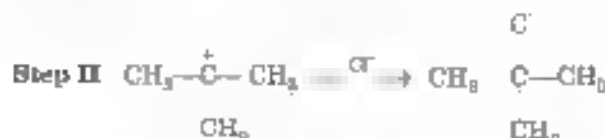


The mechanism involved in this reaction is

Step 1



3° carbocation is more stable than 1° and is predominantly formed.

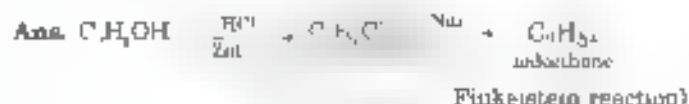


Q.29. Discuss the nature of C-X bond in the haloarenes.

Ans. In haloarenes, the carbon atom of C—X bond is sp^2 hybridised and therefore, is more electronegative than

sp^2 hybridised carbon atom in haloalkanes. Therefore, this sp^2 hybridised carbon has less tendency to release electrons to X atom of C—X bond in aryl halides and therefore, C—X bond is less polar in aryl halides as compared to alkyl halides.

Q.34, How can you obtain iodoethane from ethanol when no other iodine containing reagent except NaI is available in the laboratory ?



Q.15. Cyanide ion acts as an ambident nucleophile. From which end it acts as a stronger nucleophile in aqueous medium? Give reason for your answer.

Ans. Cyanide, $\text{C} \equiv \text{N}$, ion is an ambidentate nucleophile and can react through C as well as N end. It acts as a stronger nucleophile from carbon end because it will lead to the formation of $\text{C}-\text{C}$ bond which is more stable than $\text{C}-\text{N}$ bond forming allyl cyanide.



QUICK

MEMORY TEST



Say True or False

1. The dipole moment of CH_3F is larger than that of CH_3Cl .
2. In general, alkyl halides are more reactive than aryl halides.
3. $\text{CH}_3\text{CH}_2\text{I}$ is more reactive than $\text{CH}_3\text{CH}_2\text{Cl}$ towards KCN .
4. Carbon tetrachloride is inflammable.
5. $\text{CH}_3\text{CH}=\text{CHCl}$ is more reactive than $\text{ClCH}_2\text{CH}=\text{CH}_2$.
6. 2, 3, 4-trichloropentane has three asymmetric carbon atoms.
7. Chlorobenzene and benzyl chloride can be distinguished by boiling with aqueous KOH followed by acidification with dil HNO_3 and subsequent treatment with AgNO_3 solution.
8. Addition of BrCCl_3 to propene in the presence of peroxides gives 2-bromo-1, 1, 1-trichloro-2-methylpropane.
9. Iodide ion is a better nucleophile than bromide ion.
10. Chlorobenzene gives a white precipitate with alcoholic silver nitrate solution.
11. 2, 2-Dimethylbut-1-ene reacts with HI to form 2-iodo-2, 3-dimethylbutane and 2-iodo-2, 3-dimethylbutane.
12. Bromoethane reacts with silver nitrate to form ethyl nitrate.
13. 1, 1-Dichloroethane reacts with aqueous KOH to give ethanol.

14. Thiocethers are obtained by reacting alkyl halides with HS^- or hydrosulphide
15. Boiling point of iodobenzene is more than that of bromobenzene

 Complete the missing links

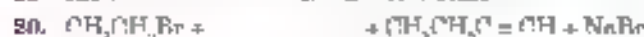
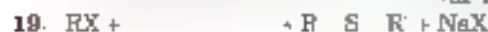
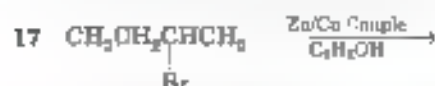
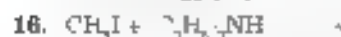
1. Isobutyl bromide is an example of alkyl halide.
2. Nitro alkanes are formed when alkyl halides react with and alkyl nitrates are formed when alkyl halides react with
3. Hydrolysis of 2-bromo-3-methylbutane gives the major product
4. Toluene reacts with Cl_2 in the presence of FeCl_3 to give
5. DDT is prepared by condensing with chlorobenzene in the presence of
6. Chlorobenzene on reduction with NiAl alloy and alcohol gives
7. Formation of phenol from chlorobenzene is an example of aromatic substitution.
8. Indobenzene on heating with copper powder forms diphenyl. This reaction is called
9. Butanenitrile can be prepared by heating with alcoholic KCN
10. With potassium cyanides, alkyl halides give while with silver cyanide, they give

11. Alkyl halides are insoluble in water because they do not form H^+ with water.

12. BHC is commercially called.



15. Chlorobenzene + Sodium + Methyl chloride \rightarrow



3. Aryl bromides can be prepared by reacting silver salt of aromatic acids with Br_2 in CCl_4 . This reaction is called *Hunsdiecker reaction* *Bart-Scramburg reaction*.



4. Dipole moment of CH_3F is *less/more* than that of CH_3Cl .

5. Dipole moment of *o*-dichlorobenzene is *less/more* than that of *m*-dichlorobenzene.

6. $\text{S}_\text{N}1/\text{S}_\text{N}2$ proceeds through the formation of a carbocation.

7. CHBrClF has *chiral/achiral* carbon atom.

8. $\text{S}_\text{N}2$ reaction occurs with *inversion of configuration/rearrangement*.

9. Out of  (I), or  (II), the compound *II/I* undergoes faster $\text{S}_\text{N}2$ reaction.

10. Iodobenzene when heated with copper powder gives *iodobenzene/diphenyl*.

11. $\text{C}_6\text{H}_5\text{Cl}$ is *less/more* reactive than $\text{C}_6\text{H}_{11}\text{Cl}$.

12. *Tetrachloroethane/tetrachloroethane* has been used as antiseptic.

C. Choose the correct alternative

1. Reaction of alkyl halide with potassium sulphate gives *isothermally/exothermally*.

2. Boiling point of *tert*-butyl bromide is *less/more* than that of *n*-butyl bromide.

Answers

Quick

MEMORY TEST



A. Say True or False

1. False 2. True 3. True 4. True 5. False

6. False: It has two chiral atoms, $\text{CH}_3\text{CH}(\text{Cl})\text{CH}(\text{Cl})\text{CH}_3$

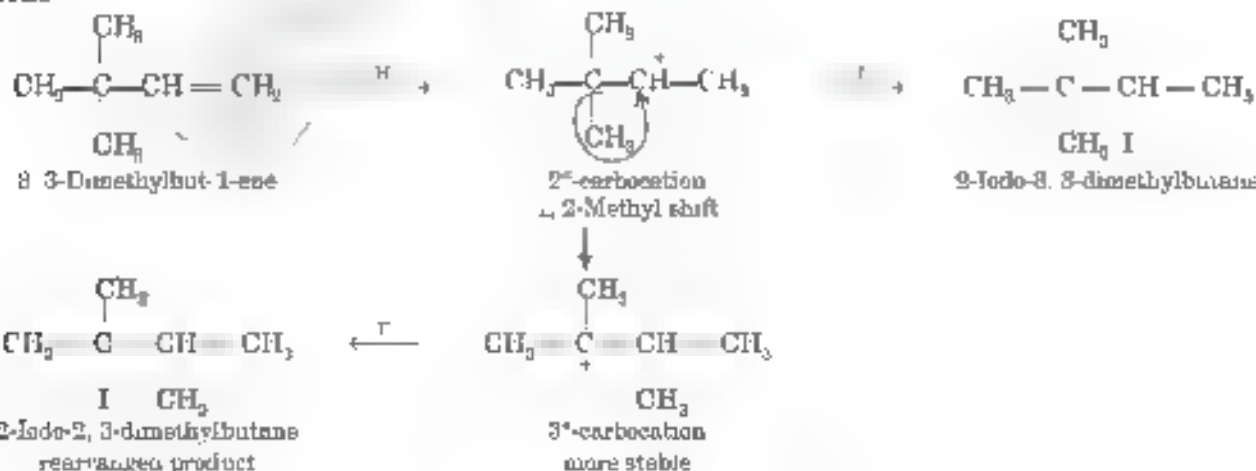
7. True



9. True

10. False. Due to resonance the $\text{C}-\text{Cl}$ bond in chlorobenzene has some double bond character. Therefore it does not want to give Cl^- ions. Hence it does not give white precipitate with alcoholic AgNO_3 .

11. True



12. False: It forms nitroethane.

13. True

14. False

15. True

B. Complete the missing links

- | | | | |
|--|---|-------------------------------|--|
| 1. primary | 2. silver nitrate, potassium nitrate | 3. 2-Methylbutan-2-ol | 4. o- and p-chlorotoluene |
| 5. Chloral, conc. H_2SO_4 | 6. benzene | 7. nucleophilic | 8. Ullmann's reagent |
| 9. n-propyl bromide | 10. alkyl cyanides, alkyl isocyanides | 11. hydrogen bonds | 12. gamma-xylene |
| 13. CH_3CHO | 14. $\text{C}_6\text{H}_5\text{CN}$, $\text{C}_6\text{H}_5\text{COOH}$ | 15. toluene | 16. $\text{CH}_2\text{N} \begin{matrix} \nearrow \text{C}_6\text{H}_5 \\ \searrow \text{C}_6\text{H}_5 \end{matrix}$ |
| 17. $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$ | 18. $\text{CH}_3\text{CH}_2\text{CN}$, $\text{CH}_3\text{CH}_2\text{CONH}_2$ | 19. $\text{Na}^+ \text{SR}^-$ | 20. $\text{NaCl} = ^-\text{H}$ |

C. Choose the correct alternative

- | | | | | |
|-------------------------|--------------------|-------------------------------|-----------|--------------|
| 1. thioethers | 2. less | 3. Hunsdiecker reaction | 4. less / | 5. less |
| 6. $\text{S}_\text{N}1$ | 7. chiral | 8. inversion of configuration | 9. I / | 10. diphenyl |
| 11. less | 12. triiodomethane | | | |

HOTS**Higher Order Thinking Skills & Advanced Level****QUESTIONS WITH ANSWERS**

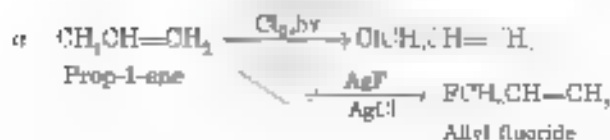
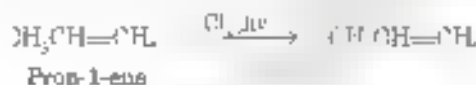
1. Why alkyl halides are generally not prepared in the laboratory by free radical halogenation of alkanes?

Ans. Free radical halogenation is not suitable method for laboratory preparation of alkyl halides because of the following reasons: (i) Because of the presence of different types of hydrogen atoms present in alkanes they give a mixture of numerous monohalogenated products whose boiling points are so close that they cannot be easily separated in the laboratory.

(ii) Substitution of more than one hydrogen atom yields polyhalogen compounds making the mixture more complex and hence difficult to separate.

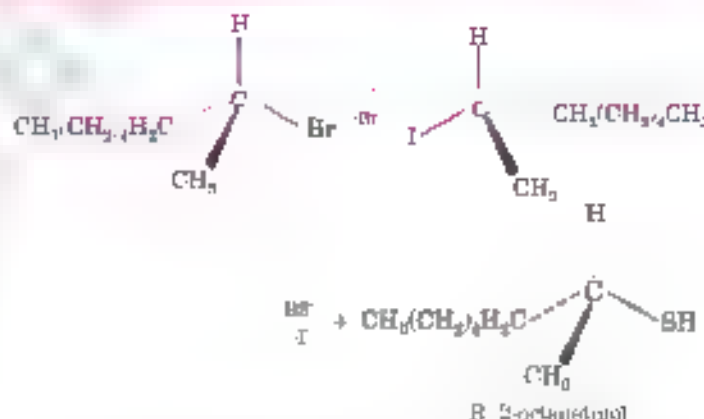
2. Propose reaction for the preparation of (i) allyl iodide and (ii) allyl fluoride from prop-1-ene.

Ans. (i) Allyl iodide is prepared from prop-1-ene as



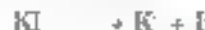
3. R-2-Bromooctane reacts with hydrogen sulphide (HS^-) ion and gives (S)-2-octanethiol with inversion of configuration at the stereocentre. Can we plan to get (R)-2-octanethiol from R-2-bromooctane?

Ans. R-2-octanethiol can be obtained from R-2-bromooctane by double inversion to get net retention of configuration. For example, an $\text{S}_\text{N}2$ reaction with I^- ion would give (S)-2-iodooctane. Then, it is reacted with HS^- to give (R)-2-octanethiol.



4. RCl is hydrolysed to ROH slowly but the reaction is rapid if a catalytic amount of KI is added to the reaction mixture. Explain.

Ans. Iodide is a powerful nucleophile and therefore it reacts rapidly with RCl to form RI .



Further I^- ion is a better leaving group than Cl^- ion and therefore, RI is more readily hydrolysed to form ROH .



5. Optically active (S)-2-iodooctane with NaI in acetone gives a product which does not show optical activity. Explain.

Ans. In this $\text{S}_\text{N}2$ reaction, iodide acts as a nucleophile as well as the leaving group. Therefore, in this reaction, iodide displaces iodide. When 2-iodooctane (I) is reacted with I^- ion, it undergoes stereochemical inversion to give 2-iodooctane (II) which is enantiomer of (I). Now (II) undergoes stereochemical inversion to give (I). This reaction is fast and occurs multiple times, each time inverting the stereochemistry. Ultimately,

Ans. (a) Reaction (i) because Br⁻ ion is a better leaving group than Cl⁻ ion.

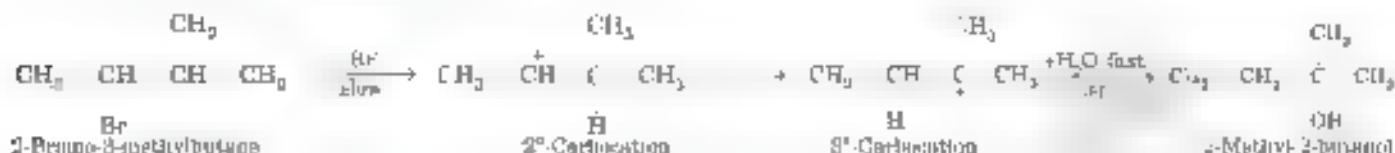
(b) Reaction (i) because the reactant is a tertiary halide. Moreover phenyl halides are not reactive in S_N1 reactions.

(c) Reaction (i) because water is more polar solvent than methanol and S_N1 reaction takes place faster in more polar solvent.

(d) Both reactions occur at the same rate because S_N1 reactions are independent of the concentration of the nucleophile.

Q2. Hydrolysis of 2-bromo-3-methylbutane (2°) gives only 2-methyl-2-butanol (3°). Explain.

Ans. During S_N1 reaction the ionization gives 2° carbocation which rearranges by a hydride shift to a more stable 3°-carbocation to form 3°-alcohol as



Q3. Haloalkanes undergo nucleophilic substitution reactions while haloarenes undergo electrophilic substitution reactions. Explain.

Ans. Haloalkanes are more polar than haloarenes. Therefore, the carbon atom carrying the halogen in haloalkanes is more electron deficient i.e. more positively charged than that in haloarene. As a result haloalkanes undergo nucleophilic substitution reactions more readily than haloarenes.

On the other hand haloarenes contain a benzene ring. Since the typical reactions of benzene are electrophilic substitution reactions, therefore haloarenes undergo electrophilic substitution reactions preferably while haloalkanes which do not contain a benzene ring do not undergo electrophilic substitution reactions.



Revision Exercises

Very Short Answer Questions Carrying mark

- How will you obtain 1-bromopropane from propane? (H.P.S.B. 2017)
- Write the structure of 2-chloro-3-methylpentane. (Assam S.B. 2017)
- Out of S_N1 and S_N2 reactions which reaction gives the inversion of configuration? (H.P.S.B. 2018)
- $$\begin{array}{c} \text{N}_2^+\text{Cl}^- \\ | \\ \text{C}_6\text{H}_5 \end{array} \xrightarrow[\text{Heat}]{\text{Cu}_2\text{Cl}_2} \quad ?$$

Complete the reaction. (H.P.S.B. 2018)
- Arrange the following alkyl halides in order of increasing reactivity towards the nucleophilic substitution S_N2^o.
 $\text{CH}_3\text{Cl} < \text{CH}_3\text{CH}_2\text{Cl} < \text{CH}_3\text{CH}_2\text{CH}_2\text{Cl} < \text{HCl}$ (Meghalaya S.B. 2018)
- Write the structural formula of 4-chloro-2-pentene.
- Write the IUPAC name of (Hr. S.B. 2018)
- Out of o-difluorobenzene and p-difluorobenzene which has higher melting point and why?
- How does iodobenzene react with copper powder? What is the name of the reaction?
- Complete the following reaction:

$$\text{C}_6\text{H}_6 \xrightarrow{\text{Cl}_2/\text{h}\nu} \quad \xrightarrow[\text{373 K}]{\text{H}_2\text{O}} \quad ? \quad (\text{Hr. S.B. 2018})$$

- A solution of KOH hydrolyses $\text{CH}_3\text{CHClCH}_2\text{CH}_3$ and $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{Cl}$. Which one of these is more easily hydrolysed? (T.S.N. 2017)
- How does chlorobenzene react with sodium in the presence of ether? What is the name of the reaction?

- Write the IUPAC name of (Hr. S.B. 2018)
- Which of the following is most reactive towards S_N2 reaction?
 CH_3Br , $\text{CH}_3\text{CH}_2\text{CH}_2\text{Br}$, $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{Br}$
- What is Wurtz reaction? (Hr. S.B. 2017)
- $$\text{H}_2\text{C}=\text{Br} + \text{AgF} \longrightarrow \text{H}_2\text{C}=\text{F} + \text{AgBr}$$

Name the reaction. (Karnataka S.B. 2014, 2018)
- Write the IUPAC name of the following compound
 $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{Br}$ (D.S.B. 2017)
- Write the IUPAC name of the following compound
 $\text{CH}_3 - \text{C}(\text{CH}_3)_2 - \text{Br}$

- Write the IUPAC name of (J.S.B. 2018)
- Write the IUPAC name of (D.S.B. 2018)
- What happens when $\text{C}_6\text{H}_5\text{Br}$ is treated with K⁺OH⁻? (D.S.B. 2018)

- Write the IUPAC name of (D.S.B. 2018)

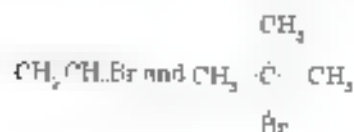
22. Write the IUPAC name of $(\text{CH}_3)_2\text{CHCH}_2\text{CH}_2\text{Cl}$
D.S.B. 2013
23. Which compound in the following pair undergoes faster $\text{S}_\text{N}1$



L.S.B. 2013

24. Arrange the following halides in order of increasing $\text{S}_\text{N}2$ reactivity
 $(\text{CH}_3)_3\text{CCl}$, CH_3Cl , CH_3Br , $\text{CH}_3\text{CH}_2\text{Cl}$, $\text{CH}_3\text{CH}_2\text{Br}$
Majhasaya S.B. 2014

25. Which would undergo $\text{S}_\text{N}2$ reaction faster in the following pair and why?



D.S.B. 2015

26. Out of $\text{CH}_3\text{CH}(\text{CH}_3)\text{CH}_2\text{Cl}$ and $\text{CH}_3\text{CH}_2\text{CH}(\text{CH}_3)\text{Cl}$, which is more reactive towards $\text{S}_\text{N}1$ reaction and why? D.S.B. 2016

27. Arrange 2-bromo-2-methylbutane, 1-bromopentane and 2-bromopentane in order of increasing $\text{S}_\text{N}2$ reactivity

Tripura S.B. 2016

28. What product is obtained when toluene is treated with Cl_2 in the presence of light? (Majhasaya S.B. 2018)

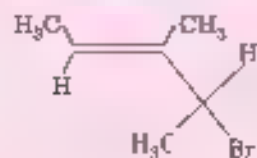
29. Write the structure of 2,4-dinitrochlorobenzene D.S.B. 2017

30. Write the structure of 1-bromo-4-chlorobut-2-ene D.S.B. 2017

31. Write the structure of 3-bromo-2-methylprop-1-ene D.S.B. 2017

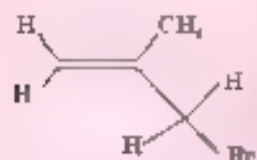
CBSE QUESTIONS

32. Give the IUPAC name of the following compound:



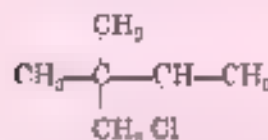
A.I.S.B. 2010

33. Write the IUPAC name of the following



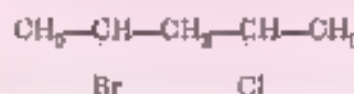
A.I.S.B. 2013

34. Write the IUPAC name of the following compound



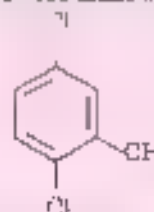
(A.I.S.B. 2013)

35. Write the IUPAC name of the following compound



A.I.S.B. 2013

36. Write the IUPAC name of following compound



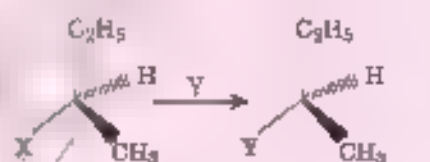
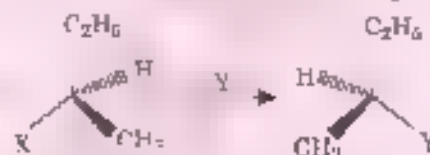
A.I.S.B. 2013

37. Identify the chiral molecule in the following pair

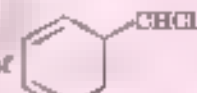
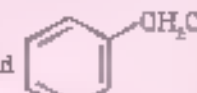




A.I.S.B. 2014

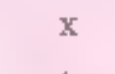

38. Which of the following two reactions is $\text{S}_\text{N}2$ and why?



A.I.S.B. 2016

39. Out of  and , which is an example of a benzylic halide? A.I.S.B. 2017

40. Out of  and , which is an example of vinylic halide? A.I.S.B. 2017

41. Out of  and , which is an example of allylic halide? A.I.S.B. 2017

MCQs from State Boards' Examinations

42. $\text{C}_2\text{H}_5\text{Cl}$ on heating with alcoholic KOH will produce
a) $\text{C}_2\text{H}_5\text{OH}$ (b) C_2H_4
c) C_2H_6 (d) C_2H_2 (Jharkhand S.B. 2013)
43. Alkyl halides are less soluble in water because they have
a) Low melting point.
b) Do not form H-bond with H_2O
c) Viscous in nature
d) Have very strong C-X bond (H.P. S.B. 2014)
44. Among the following which one is chlorine containing insecticide?
a) DDT (b) Freon
c) Phosgene (d) Iodofarm (Kerala S.B. 2015)

45. The boiling points of haloalkanes follow the order

- (a) $RI > RBr > RCl$
 (b) $RCl > RBr > RI$
 (c) $RI > RCl > RBr$
 (d) $RBr > RI > RCl$

(Nagaland S.B. 2015)

46. The chiral compound is

- (a) 3-chloropentane (b) Propene
 (c) 2-chloropropane (d) 2-chlorobutane

(Hr S.B. 2015)

47. Which of the following has highest dipole moment in the following?

- (a) CH_3F (b) CH_3Cl
 (c) COI_4 (d) CH_3I (Hr S.B. 2015)

48. Which of the following is not a polyhalogen compound?

- (a) Chloroform (b) Freon
 (c) Carbon tetrachloride (d) Chlorobenzene

(Kerala S.B. 2016)

49. The ease of dehydrohalogenation of alkyl halides with alcoholic KOH is

- (a) $3^\circ < 2^\circ < 1^\circ$ (b) $3^\circ > 2^\circ > 1^\circ$
 (c) $3^\circ < 2^\circ > 1^\circ$ (d) None of these

(Hr S.B. 2017)

50. Alkyl halides are prepared from alcohol by treating with

- (a) $HCl + ZnCl_2$
 (b) $H_2SO_4 + KI$
 (c) $NaCl + H_2SO_4$
 (d) None of these

(Hr S.B. 2017)

51. Organic compound which shows complete stereochemical inversion during S_N2 reaction is

- (a) CH_3Cl
 (b) $CH_3CH_2CH_2Cl$
 (c) $(CH_3)_2CHCl$
 (d) None of these

(Hr S.B. 2017)

52. Which of the following reaction is most suitable for the preparation of n-propylbenzene?

- (a) Friedel-Crafts alkylation
 (b) Wurtz reaction
 (c) Wurtz-Fittig reaction
 (d) Grignard reaction

(Manipal S.B. 2017)



This reaction is:

- (a) Stephen (b) Sandmeyer's
 (c) Fittig (d) Wurtz-Fittig

(Hr S.B. 2018)

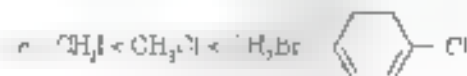
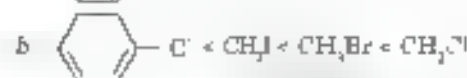
54. In the given alkyl halides which one has minimum boiling point?

- (a) C_2H_5F (b) C_2H_5I
 (c) C_2H_5Cl (d) C_2H_5Br (Hr S.B. 2018)

55. S_N2 reaction will be fastest in

- (a) CH_3Br (b) CH_3Cl
 (c) CH_3CH_2Cl (d) $(CH_3)_2CHCl$ (Hr S.B. 2018)

56. For the compounds, CH_3Cl , CH_3Br and CH_3I which of the following is the correct order of C-halogen bond length?



(WB S.B. 2018)

Short Answer Questions (carrying 2 or 3 marks)

- How is ethyl bromide converted into
 (a) ethanol / (b) ethyl acetate
 (c) diethyl amine (d) propanoic acid?
- How will you convert
 (i) n-propyl bromide to iso-propyl bromide
 (ii) 1-bromopropane into propene
 (iii) 2-propanol into 1-bromopropane
 (iv) 2-chlorobutane into butanol?
- How will you distinguish between
 (i) Vinyl chloride and ethyl chloride
 (ii) Chlorobenzene and cyclohexyl chloride
 (iii) Ethyl chloride and ethyl bromide?
- (a) Haloarenes undergo electrophilic substitution reaction at ortho and para position. Explain.
 (b) Complete the following reaction:
 $CH_3Br \xrightarrow{\text{Dry ether}} A \xrightarrow{Na, C_2H_5OH} B$

(Mauritius S.B. 2015)

5. Write the following reactions.

- (i) Swarts reaction
 (ii) Sandmeyer reaction
 (iii) Wurtz-Fittig reaction (Hr S.B. 2018)

6. (a) How are the following conversions be carried out

- (i) Benzene to diphenyl
 (ii) Aniline to chlorobenzene
 (b) Why is trichloromethane stored in dark coloured bottles? Give reason with related equation.
 (Uttarakhand S.B. 2015)



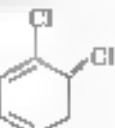


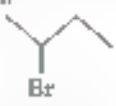



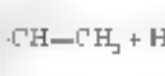
7. Explain as to why haloarenes are much less reactive than haloalkanes towards nucleophilic substitution reactions.

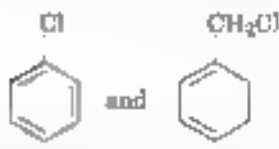

(T.S.B. 2009, A.I.S.B. 2009, Hr S.B. 2018, 2014, 2016, 2019, H.P.S.B. 2017, 2018, Kerala S.B. 2017, Nagaland S.B. 2017)

Or

Which compound in each of the following pairs will react faster in S_N2 reaction with OH^- ? Why?

- (i) CH_3Br or CH_3I
 (ii) CH_3CH_2Cl or CH_3Cl (P.S.B. 2008)

8. Write the equations for the steps in S_N1 mechanism of the conversion of tert-Butyl bromide into tert-Butyl alcohol.
- Explain Fittig reaction.
 - Name the reagent used in the dehydrohalogenation of haloalkanes. (Karnataka S.B. 2018)
9. a) State one use each of DDT and iodoform.
b) Which compound in the following couples will react faster in S_N2 displacement and why?
(i) 1-Bromopentane or 2-bromopentane
(ii) 1-Bromo-2-methylbutane or 2-bromo-2-methylbutane (D.S.B. 2016)
10. Explain why
(i) The dipole moment of chlorobenzene is lower than that of cyclohexyl chloride
(ii) Grignard reagent should be prepared under anhydrous conditions.
(iii) Haloalkanes though polar are immiscible with water? (Hr. S.B. 2011, H.P. S.B. 2018)
11. Answer the following
Haloalkanes easily dissolve in organic solvents, why?
a) What is known as racemic mixture? Give an example.
b) Of the two bromoderivatives C_4H_9Br and C_4H_9Br which one is more reactive in S_N1 substitution reaction and why? (D.S.B. 2011)
12. Although chlorine is an electron withdrawing group, yet it is ortho-para-directing in electrophilic aromatic substitution reactions. Explain why is it so? (D.S.B. 2018)
13. Identify A and B
- a) $CH_3CH=CH_2 + HBr \xrightarrow{A} B \xrightarrow{aq. KOH} C$
- b)  $\xrightarrow{HBr} A \xrightarrow{aq. KOH} B$ (Maurand S.B. 2018)
14. (a) Explain why thionyl chloride ($SOCl_2$) method is preferred for preparing alkyl chlorides from alcohols.
b) For isomeric haloalkanes, the boiling point decreases with branching of chain. Why? (Meghalaya S.B. 2018)
15. Identify the major product in the following reactions
- $CH_3CH=CH_2 + HCl \rightarrow CH_3CH_2CH_2Cl + CH_3CHClCH_3$
-  $\xrightarrow{\text{Anhyd. } FeCl_3}$  +  (Assam S.B. 2018)
16. Write chemical reactions to prepare the followings
a) DDT from chlorobenzene
b) Freon-12 from carbon tetrachloride. (Uttarakhand Board 2014)
17. (a) Which alkyl halide from the following pair is chiral and undergoes faster S_N2 reaction?
-  
- b) Out of S_N1 and S_N2 , which reaction occurs with
(i) Inversion of configuration
(ii) Racemisation. (D.S.B. 2014)
18. Draw the structure of major monohalo product in each of the following reactions
-  \xrightarrow{HBr} 
-  $+ HBr \xrightarrow{\text{Peroxide}}$  (D.S.B. 2014)
19. a) What is the condition to be satisfied for a compound to be chiral?
b) Under what conditions 2-methylpropene can be converted into isobutyl bromide? 1-bromo-2-methylpropane by hydrogen bromide? Write the correct reaction involved.
c) How will you carry the following conversion?
- $CH_3CH_2CH_2OH \rightarrow CH_3CH_2CH_2Cl$
- (Meghalaya S.B. 2016)
20. Explain S_N2 reaction mechanism of haloalkane. Arrange the reactivity of 1°, 2° and 3° haloalkanes towards S_N2 reaction. (Nagaland S.B. 2015)
21. a) Explain why haloarenes undergo electrophilic substitution reactions at ortho and para positions only. (Maurand S.B. 2018)
b) The p-isomer of dichlorobenzene has higher melting point than its ortho and meta-isomers. Explain. (Maurand S.B. 2018)
22. (a) Complete the reaction
 $CH_3CH_2Br + KOH \xrightarrow{alc.} \rightarrow$
b) Explain why the use of chloroform as anesthetic is decreasing.
c) What happens when bromobenzene is treated with magnesium in the presence of dry ether? (H.P. S.B. 2015)
23. How will you convert the following:
(a) Propene into isopropyl bromide
Propene into n-propyl bromide (H. S.B. 2014)
24. Explain the following reactions
a) Fittig reaction
b) β -Elimination reaction (H.P.)
- Discuss S_N1 and S_N2 reactions with suitable examples. (Hr. S.B. 2016)

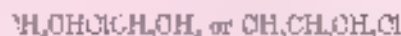
25. (a) Alkyl halides react with AgNO_3 and KNO_3 to give R-NO_2 and R-ONO respectively. Why?
 (b) Haloarenes are insoluble in water but are soluble in benzene. Why? *Pb. S.B. 2015*
26. What happens when ethyl bromide reacts with
 (a) AgNO_3
 (b) AgCN etc.?
 (b) The *p*-isomer of dichlorobenzene has higher melting point than *o*- and *m*- isomer. Why? *Pb. S.B. 2015*
27. (a) Haloalkanes react with potassium cyanide (KCN) to give alkyl cyanide but gives alkyl isocyanide with silver cyanide (AgCN).
 (b) Why are haloarenes more stable than haloalkanes? *HP S.B. 2015*
28. Give reasons.
 (a) *n*-Butyl bromide has higher boiling point than *t*-butyl bromide.
 (b) Racemic mixture is optically inactive.
 (c) The presence of nitro group ($-\text{NO}_2$) at *o/p* positions increases the reactivity of haloarenes towards nucleophilic substitution reactions. *D.S.B. 2015*
29. (a) In  identify the compound which will undergo $\text{S}_{\text{N}}1$ reaction faster and why?
 (b) Explain the following:
 i. ambident nucleophile
 ii. asymmetric carbon *(Hr. S.B. 2018)*
30. Explain $\text{S}_{\text{N}}2$ reaction mechanism of haloalkanes. *Nagaland S.B. 2018*
31. (a) In the following halogen compounds, which one will readily undergo $\text{S}_{\text{N}}2$ reaction:
 $\text{CH}_3\text{CH}_2\text{-Cl}$ $\text{CH}_3\text{C(CH}_3)_2\text{-Cl}$
 (b) Complete the following reaction:
 $\text{CH}_3\text{Br} + \text{C}_2\text{H}_5\text{ONa} \rightarrow$ *(Assam S.B. 2018)*
32. (a) Aryl halides are less reactive in nucleophilic substitution reactions.
 (i) Write any two reasons for less reactivity.
 ii. Give one example for nucleophilic substitution reactions of aryl halides.
 (b) Write a method for the preparation of alkyl halides.
 (c) Which of the following is not a polyhalogen compound?
 i. Chloroform (ii) Freon
 iii. Carbon tetrachloride (iv) Chlorobenzene *Kerala S.B. 2018*
33. (a) Give two methods of preparation of haloalkanes.
 (b) Give two uses of iodoform. *Jammu S.B. 2018*
34. (a) Write DDT structure. Give harmful effects of DDT.
 (b) Write Wurtz-Fittig reaction. *(H.P.S.B. 2018)*
35. (a) What are ambident nucleophiles? Explain with an example.
 (b) Write Sandmeyer reaction. *H.P.S.B. 2018*
36. Give reasons.
 (i) C-Cl bond length in chlorobenzene is shorter than C-Cl bond length in $\text{CH}_3\text{-Cl}$.
 (ii) The dipole moment of chlorobenzene is lower than that of cyclohexyl chloride.
 (iii) $\text{S}_{\text{N}}1$ reactions are accompanied by racemisation in optically active alkyl halides. *L.S.B. 2018*
37. (a) Arrange the following in their reactivity towards $\text{S}_{\text{N}}2$ reaction and give the reason for your answer: Primary halide, secondary halide, tertiary halide and methyl halide.
 (b) Write the chemical reaction involved in the conversion of propene to propyne. *Mizoram S.B. 2017*
38. Identify A and B in the following two reactions:
 (i) $\text{A} + \text{Na} + \text{CH}_3\text{Cl} \xrightarrow{\text{ether}} \text{C}_6\text{H}_5\text{-CH}_3 + \text{NaCl}$
 (ii) $\text{C}_6\text{H}_5\text{-Cl} + ^\text{t}\text{Na} \xrightarrow{\text{DMSO}} \text{B} + 2\text{NaCl}$ *Assam S.B. 2017*
39. Write the following reactions:
 (i) Wurtz reaction (ii) Sandmeyer's reaction
 (iii) Ullmann reaction *Pb.S.B. 2017*
40. (a) Why are haloarenes more stable than haloalkanes?
 (i) Alkyl halides react with AgNO_3 to give R-NO_2 or R-ONO . Explain. *(Pb.S.B. 2017)*
41. (a) What is DDT?
 (ii) Complete the reaction:
 $\text{CH}_3\text{CH}_2\text{OH} + \text{SOCl}_2 \xrightarrow{\text{pyridine}} ? + ? + ?$ *Nagaland S.B. 2017*
42. (a) In the following pair of halogen compounds, which would undergo $\text{S}_{\text{N}}1$ reaction faster?

 (b) Explain why Grignard reagents should be prepared under anhydrous conditions.
 (c) Starting from benzene, prepare diphenyl in not more than two steps. *Meghalaya S.B. 2017*
43. (a) Complete the reaction:
 (i) $\text{CH}_3\text{CH}_2\text{Br} \xrightarrow{\text{AgCN}}$
 (ii) $\text{CH}_3\text{CH}_2\text{Br} \xrightarrow[\text{Dry ether}]{\text{Na}}$
 (b) During the β -elimination reaction of 2-bromopentane in an alcoholic solution of KOH results pent-2-ene as major product and pent-1-ene as minor product. State the rule to explain the reaction. *Kerala S.B. 2018*

CBSE QUESTIONS

44. How would you differentiate between S_N1 and S_N2 mechanisms of substitution reactions? Give one example of each. *A.I.S.B. 2016, Hr S.B. 2018*

45. (a) What is meant by chirality of a compound? Give an example

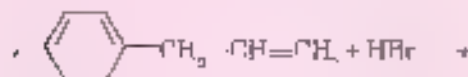
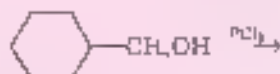
(b) Which one of the following compounds is more easily hydrolysed by KOH and why?



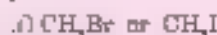
(c) Which one undergoes S_N2 substitution reaction faster and why?



46. (a) Draw the structures of major monohalo products in each of the following reactions



(b) Which halogen compound in each of the following pairs will react faster in S_N2 reaction



A.I.S.B. 2015

47. (a) How would you convert the following:

(i) Prop-1-ene to 1-fluoropropane

(ii) Chlorobenzene to 2-chlorotoluene

(b) Write the main product when

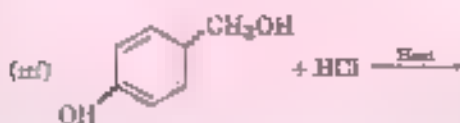
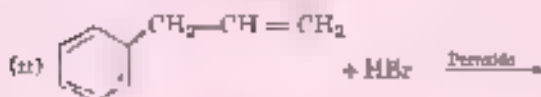
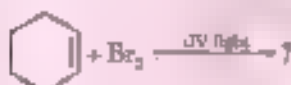
(i) n-Butyl chloride is treated with alcoholic KOH

(ii) 2, 4, 6-trinitrochlorobenzene is subjected to hydrolysis

(iii) methyl chloride is treated with AgCN

A.I.S.B. 20

48. Write the major monohalo product(s) in each of the following reactions:



A.I.S.B. 2010

49. Following compounds are given to you:

2-Bromopentane, 2-Bromo-2-methylbutane, 1-Bromopentane

(i) Write the compound which is most reactive towards S_N2 reaction.

(ii) Write the compound which is optically active

(iii) Write the compound which is most reactive towards β -elimination reaction. *D.S.B. 2017*

50. Out of chlorobenzene and benzyl chloride, which one gets easily hydrolysed by aqueous NaOH and why?

A.I.S.B. 2018

51. (a) Identify the chiral molecule in the following pair



(b) Write the structure of the product when chlorobenzene is treated with methyl chloride in the presence of sodium metal and dry ether

(c) Write the structure of the alkene formed by dehydrohalogenation of 1-bromo-1-methylcyclohexane with alcoholic KOH

A.I.S.B. 2018

Long Answer Questions — carrying 5 marks

1. (a) For the preparation of alkyl chlorides from alcohols, thionyl chloride ($SOCl_2$) is preferred. Give reason.

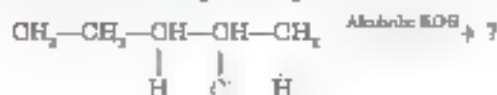
(b) Haloalkenes undergo β -elimination reaction in the presence of alcoholic potassium hydroxide

(i) Which is the major product obtained by the β -elimination of 2-bromopentane?

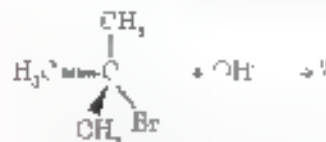
(ii) Name the rule which leads to the product in the above elimination reaction.

(c) Write the chemical equation for the preparation of toluene by Wurtz-Fittig reaction. *Kerala S.B. 2018*

2. (a) Identify all possible alkenes that would be formed on dehydrohalogenation of 2-chloropentane with alcoholic KOH. Also identify the major alkene



(b) Write the products of the following reaction which is a first-order reaction giving the steps involved



(c) Draw the structures of major monohalo products in each of the following reactions



3. Explain the following reactions:

- Balz Schiemann reaction
- Wurtz reaction
- Ullmann reaction
- Give two uses of chloroform
- The dipole moment of chlorobenzene is lower than that of cyclohexyl chloride. Explain. (Pb. S.B. 2014)

4. Write short notes on the following

- Finkelstein reaction
- Markovnikov's rule
- Hunsdiecker reaction

Or

- An organic compound 'A' having molecular formula C_4H_9 on treatment with dil. H_2SO_4 gives 'B'. 'B' on treatment with conc. HCl and anhydrous $ZnCl_2$ gives secondary halide 'C'. Write all the reactions and identify A, B and C.

- Convert ethyl chloride into methyl chloride

H.P.S.B. 2014

5. Write short notes on the following

- Sandmeyer's reaction
- Friedel-Craft's alkylation
- Anti-Markovnikov's rule

Or

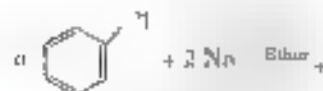
- A hydrocarbon 'A' (C_4H_8) is added with HBr in accordance with Markovnikov's rule to give compound 'B' which on hydrolysis with aqueous alkali forms tertiary alcohol 'C' ($C_4H_{10}O$). Identify A, B and C.

- Convert chlorobenzene into phenol. H.P.S.B. 2014

- Write the equations for the steps in S_N1 mechanism of the conversion of tert-butyl bromide into tert-butyl alcohol

- Haloarenes are less reactive towards nucleophilic substitution reactions than haloalkanes. Give a reason.

6. Complete the following equations



Karnataka Board 2014

- How will you differentiate between S_N1 and S_N2 reactions?

- Why does the treatment of alkyl chloride with silver nitrate form nitroalkane and with potassium nitrite form alkyl nitrite? (Pb. S.B. 2018)

8. a. An ambident nucleophile is:

- Ammonia (ii) Ammonium ion
- Chloride ion (iv) Nitrite ion

- Haloalkanes and haloarenes are organohalogen compounds.

- Suggest a method for the preparation of alkyl chloride.

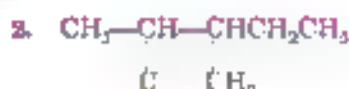
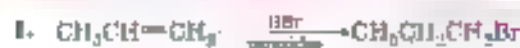
- Aryl halides are less reactive towards nucleophilic substitution reactions. Give reasons.

Kerala S.B. 2017

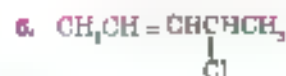
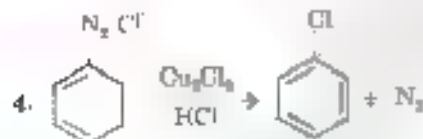
Hints & Answers

for Revision Exercises

Very Short Answer Questions



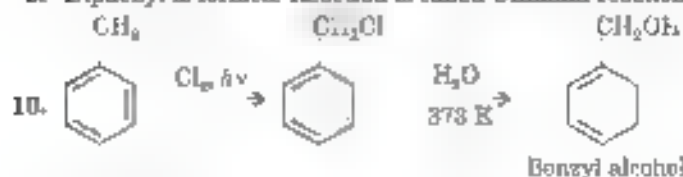
3. S_N2



7. 1-chloro-1-phenylmethane

8. *p*-dichlorobenzene. The *p*-isomer is more symmetrical and therefore, fits better into its crystal lattice. As a result, the intermolecular forces are larger than the corresponding *o*-isomers. Hence *p*-isomer has higher melting point.

9. Diphenyl is formed. Reaction is called Ullmann reaction.



12. Diphenyl is formed. The reaction is Fittig reaction.

13. 1-chloro-2-phenylethane



16. Swarts reaction.

18. 3-Bromo-2-methylpropene

20. Ethanenitrile is formed. $\text{CH}_3\text{Br} + \text{KCN}$

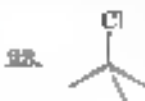
17. 2, 2-Dimethyl-1-bromopropane

19. 4-chloropent-1-ene



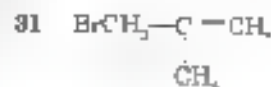
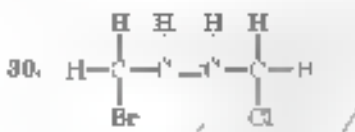
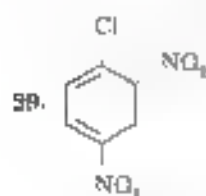
21. 4-Bromo-4-methylpent-2-ene.

22. 2-Chloro-3-methylbutane

24. $(\text{CH}_3)_3\text{CCl} < (\text{CH}_3)_2\text{CHCl} < \text{CH}_3\text{CH}_2\text{Cl} < \text{CH}_3\text{Cl} < \text{CH}_3\text{Br}$ 25. $\text{CH}_3\text{CH}_2\text{Br}$ 26. $\text{CH}_3\text{CH}_2\text{CHClCH}_3$

27. 2-bromo-2-methylbutane < 2-bromopentane < 1-bromopentane

28. Benzyl chloride



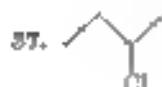
32. 4-Bromo-3-methylpent-2-ene

33. 3-Bromo-2-methylpropene

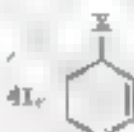
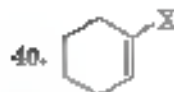
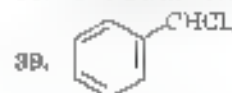
34. 3-Chloro-2, 2-dimethylbutane

35. 2-Bromo-4-chloropentane.

36. 1 + Dichlorotoluene



38. (c)



42. (b)

43. (b)

44. (a)

45. (a)

46. (d)

47. (b)

48. (d)

49. (b)

50. (a)

51. (a)

52. (a)

53. (d)

54. (a)

55. (a)

56. (a)

Competition File

Additional Useful Information and Objective Questions

ADDITIONAL USEFUL INFORMATION

► DISSYMMETRY - CONDITION FOR ENANTIOMERISM

Dissymmetry is an essential condition for optical activity. In other words, the molecules which are not symmetrical will form non-superimposable mirror image called enantiomers.

Thus, the essential criterion for chirality of a molecule i.e. to form enantiomers non-superimposable mirror images is the dissymmetry (absence of plane of symmetry). In other words, the fundamental condition for enantiomerism is dissymmetry.

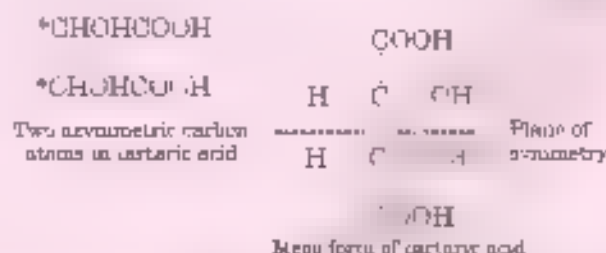
These enantiomers are represented as d- or + and l- or - . It may be noted that the enantiomers are due to non-superimposability of mirror images and thus gives them the property of optical activity. Therefore enantiomers are also referred as optical isomers.

Competition File

The enantiomers have identical chemical properties, and therefore, they form same products. However, they differ in the reactivity towards other optically active substances. For example, (+)-lactic acid and (–)-lactic acid have similar chemical properties. When these enantiomers are treated with optically active *sec*-butyl alcohol, both form esters but their rates of reaction are very different.

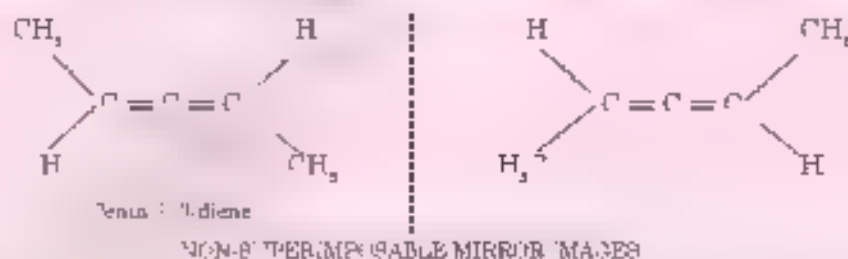
It may be noted that the fundamental condition for enantiomerism is dissymmetry. A molecule which is dissymmetric will exhibit enantiomerism and the enantiomers have dissymmetry. Thus, *dissymmetry is necessary and sufficient condition for enantiomerism*.

However, the presence of asymmetric carbon atom is important for enantiomerism but it is not the essential and sufficient condition. There are certain molecules which contain more than one asymmetric carbon atoms but are optically inactive. For example, *meso* form of tartaric acid.



In this molecule, there is a plane of symmetry so that one half of the molecule is the mirror image of the other half. As a result, it is **optically inactive**. An optically inactive molecule whose molecule is superimposable on its mirror image, despite of the presence of asymmetric carbon atoms, is known as a **meso compound**. Such a molecule can be recognised by the fact that it possesses a mirror plane which divides the molecule into two halves which are mirror image of each other. Therefore, optical inactivity of a meso compound is due to **internal compensation**. The two halves of the molecule rotate the plane of polarized light in opposite directions and hence cancel the effect of each other.

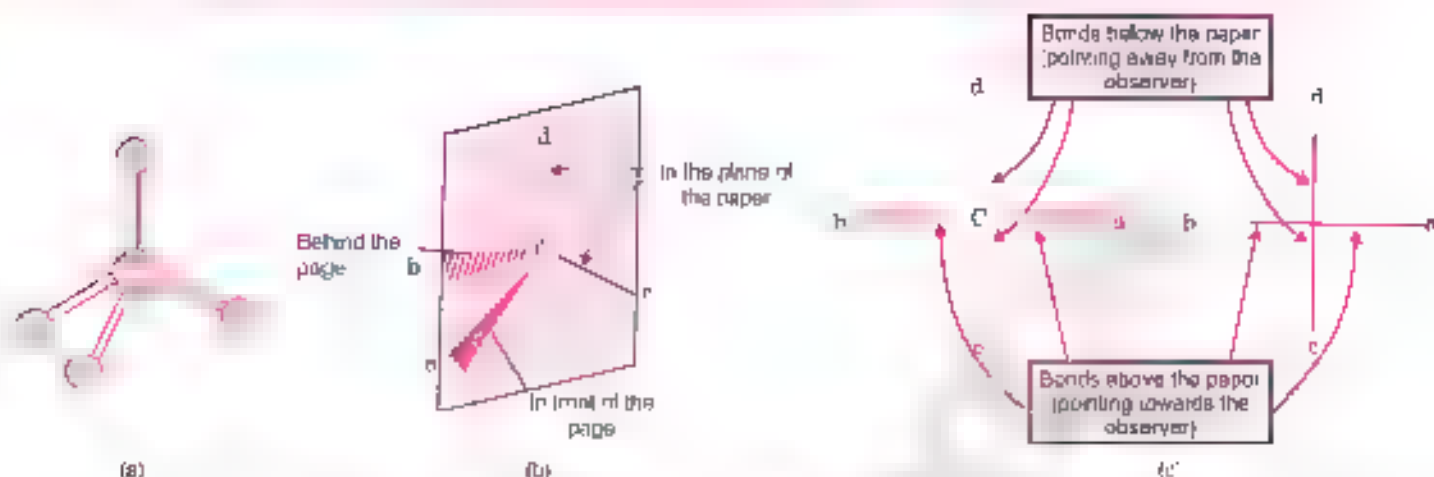
Similarly, there are molecules which do not contain any asymmetric carbon atom but are enantiomers. For example, *cis*-2-butene exists in two forms which are non-superimposable mirror images and are optically active.



CONFIGURATIONS AND FISCHER PROJECTIONS

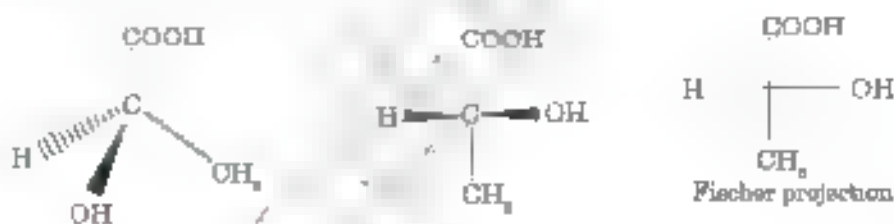
The arrangement of atoms that characterizes a particular stereoisomer is called its **configuration**. It is very difficult to draw three dimensional arrangement of atoms or the configuration of a molecule on a paper (two dimensional). Therefore, various graphic methods have been proposed. The simplest method is the **Wedge formula**. In this representation, a tetrahedral molecule with four atoms or groups *a*, *b*, *c* and *d* bonded to *x*, can be represented by a **Wedge formula**. A solid wedge (or a heavy line) represents a bond projecting above the plane of the paper, i.e. bond pointing towards you, and a dashed wedge (or a dashed line) represents a bond below the plane, i.e. bond pointing away from you. Solid lines (or continuous lines) represent bonds in the plane of the paper. These representations are shown ahead.

Competition File



A simplification of Wedge formula is Fischer projection. In Fischer projection, a tetrahedral carbon atom is represented by two crossed lines. In this projection, the chiral carbon is at the centre of intersection of the horizontal and vertical lines and by convention, it is not shown in the Fischer projection. The four groups attached to the chiral carbon are placed on the four ends of the cross. The horizontal lines represent bonds coming out of the plane of the paper (directed towards the viewer) and the vertical lines represent bonds going back from the plane of the paper away from the viewer. The carbon chain is usually drawn vertically with C-1 at top. For example, the molecule *abcd* may be represented as shown before in Fig. (c).

For example, R-acetic acid can be drawn as



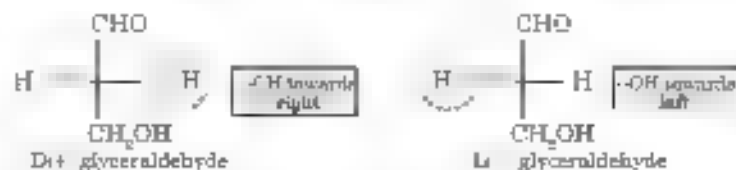
NOMENCLATURE OF STEREOISOMERS

There are two commonly used nomenclature systems or conventions for stereoisomers.

1. D and L-system
2. R and S-system.

1. D and L System of Nomenclature

This is an older system of denoting absolute configuration of enantiomers. The main chain of the carbon containing the chiral centre is arranged vertically on the page with the carbon in the higher oxidation state (the one with more C=O bond) on the top. The vertical bonds extend behind the plane of the page and the horizontal bonds project in front of the plane of the page. When the molecule is arranged in this manner, its configurations are designated relative to the glyceraldehyde chosen as standard. The two enantiomers of glyceraldehyde were designated by D and L symbols as.



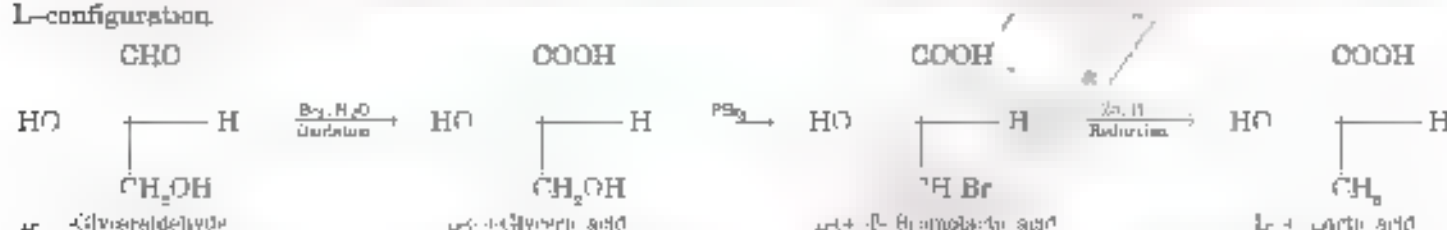
The D-configuration has OH attached to the carbon adjacent to CH_2OH group on **right** while L-configuration has OH attached to the carbon adjacent to CH_2OH group on **left**. Any compound that can be prepared or converted into D-glyceraldehyde will belong to **D-series** while any compound that can be prepared from or converted into L-glyceraldehyde will belong to **L-series**. This is based on the general principle that if a reaction does not involve the cleavage of a bond to the chiral centre, then the configuration about that chiral centre is retained. For

Competition File

example, D-+ glyceraldehyde can be converted into D-+ glyceric acid by oxidation with Br_2 water and therefore the configuration of glyceric acid obtained will be D.

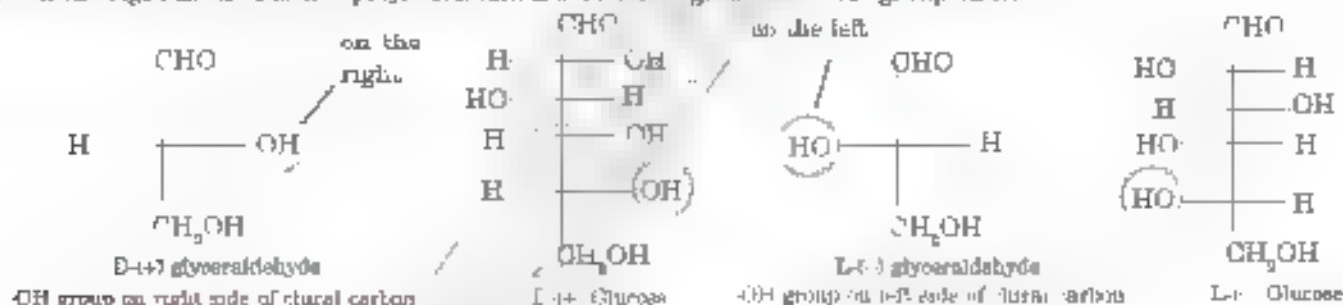


Similarly, +lactic obtained from L-+ glyceraldehyde by the following sequence of reactions is assigned L-configuration.



It may be noted that D- and L- do not represent dextrorotatory or levorotatory. The optical activity of the molecule is represented by + and - which represent the direction of rotation of plane polarized light whether dextrorotatory or levorotatory. This method has certain limitations. For example, sometimes the same compound can be correlated by sequences of reactions to a known D- compound and by a different sequence of reactions to a known L- compound.

However, this method is still popular in biochemistry and biology and is used to indicate the configuration of compounds such as sugars, amino acids, etc. The D-series of sugars are those which have -OH group on the highest number stereo centre on the right in the Fischer projection and L-series of sugars have -OH group on left.



This method has been replaced by R and S method.

2. R and S-system of Nomenclature

The different stereoisomers of a molecule can be expressed in terms of R and S configuration. This method was proposed by C. D. Ingold and Prelog. This method has been accepted by IUPAC. It is based on the assignment of priorities to the atoms or groups attached to the central carbon. The priorities can be assigned on the basis of the following rules.

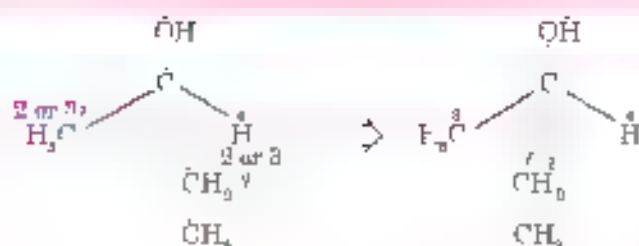
Sequence rules

1. If the four atoms attached to the chiral carbon atoms are all different, priority depends upon atomic number, with the atom having higher atomic number getting higher priority and the atom having lowest atomic number getting lowest priority. If two atoms are composed of the same element, the atom of higher mass number has the higher priority. For simplicity, these priorities may be written as 1, highest; 2, 3, 4, lowest. For example,

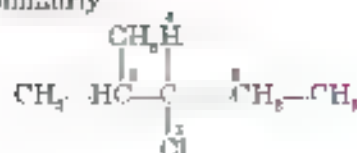


2. If the relative priority of two groups cannot be decided by rule 1 on the basis of the atomic number of the atoms that are directly attached to the asymmetric carbon, then the next atoms are considered for priority assignment. For example, if CH_3 and C_2H_5 are attached, C_2H_5 gets priority because atoms attached to first C atom are C, H and H whereas in CH_3 group, atoms attached are H, H and H. For example,

Competition File

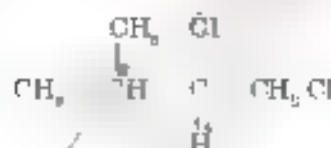


Similarly



3-Chloro-2-methylpentane

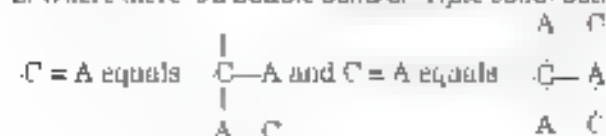
(C, C, H of isopropyl) take priority over (C, H, H of ethyl)



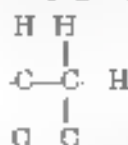
1,2-Dichloro-3-methyl butane

(Cl, H, H of isopropyl group) get priority over (C, C, H of isopropyl group) because Cl has higher atomic number than carbon.

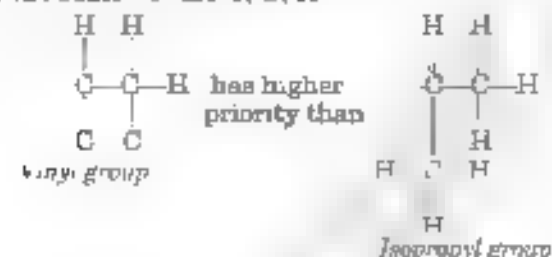
3. Where there is a double bond or triple bond, both atoms are considered to be duplicated or triplicated. For example,



For example, $\text{CH}=\text{CH}_2$ is treated as vinyl group

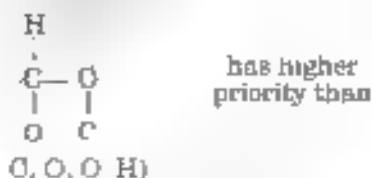


Thus, vinyl group gets priority over isopropyl group. $\text{H}, \text{H}, \text{H}$ because at the third set of atoms, the vinyl group has $\text{H}, \text{H}, \text{H}$ while isopropyl group along either branch has $\text{H}, \text{H}, \text{H}$. (At the first and second set of atoms both groups are the same: C and $\text{C}, \text{C}, \text{H}$)

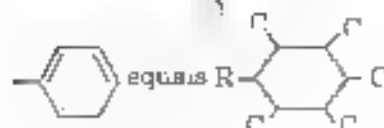


H

Similarly, $\text{C}=\text{O}$ has higher priority than CH_2OH

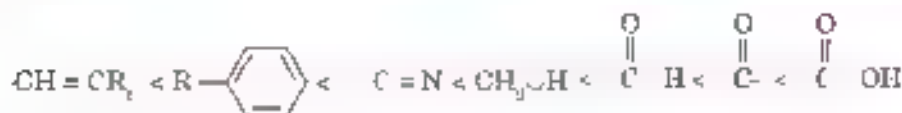


Similarly $\text{R}-\text{C}(\text{OH})=\text{C}(\text{H})-\text{R}$ equals $\text{R}-\text{C}(\text{H})=\text{C}(\text{H})-\text{R}$ equals $\text{R}-\text{CH}=\text{CH}-\text{R}$ equals $\text{R}-\text{CH}=\text{CR}_2$ equals $\text{R}-\text{CH}=\text{CR}_2$ and



Competition File

By this rule we get the following increasing order of priority



Third rule is not commonly used.

Steps for Nomenclature

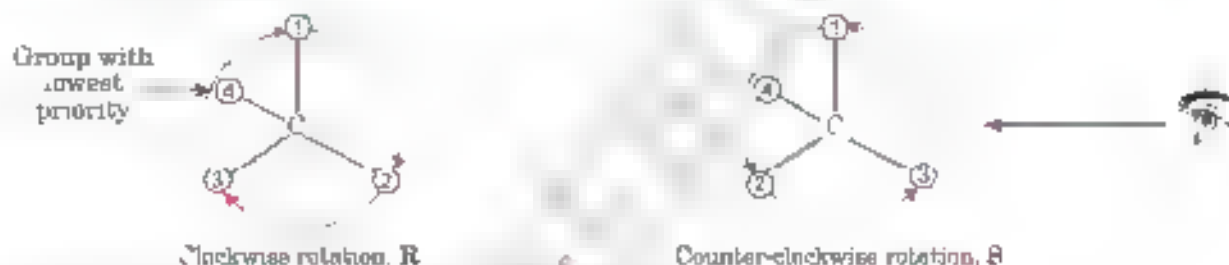
This method involves the following steps

Step 1 Identify the centre or centres of chirality in the molecule.

Step 2. The four atoms or groups of atoms joined to the chiral carbon atom are assigned a sequence of priority by the sequence rules. These are also called CIP rules as discussed above.

Step 3. After assigning the priorities to the four groups or atoms attached to the chiral C atom, the molecule is visualized to be in a position where the atom or group of atoms of lowest priority (4) is directed away from us. Then we trace the path from the atom or group in the decreasing order of priorities (i.e. from 1 to 2 to 3).

In doing so, if an eye travels in a clockwise direction the configuration is specified as **R** (for Latin word *rectus* meaning right). However, if the eye moves in counter-clockwise direction, the configuration is specified as **S** (for Latin word *sinister* meaning left).



Let us consider a simple molecule 1-bromo-2-chloroethane, CH_3CHClBr

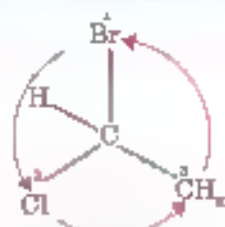


The molecule is now oriented so that the lowest priority group, i.e. H is directed away from us.

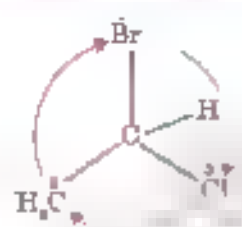


Competition File

Now trace the path from the atom or group in decreasing order of priorities i.e. from 1 \rightarrow 2 \rightarrow 3 as

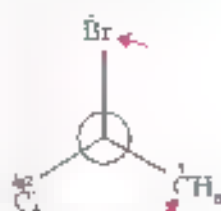


Counter-clockwise rotation
S-configuration

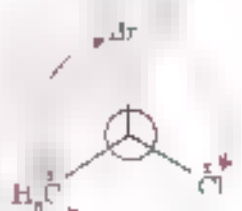


Clockwise rotation
R-configuration

This may also simply be viewed as

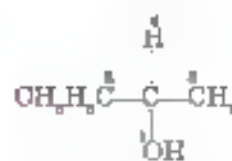


Counter-clockwise
S-configuration



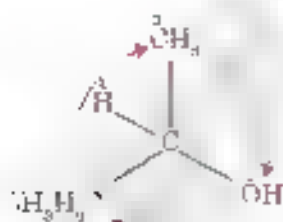
Clockwise
R-configuration

Let us consider some more examples

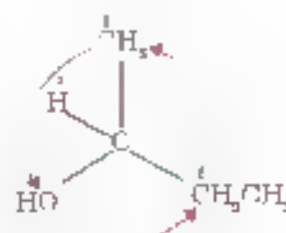


Butan-2-ol

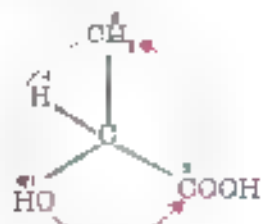
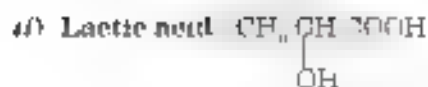
Priority order OH, CH_3CH_2 , CH_3 , H



Clockwise, **R**

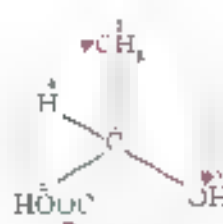


Counter-clockwise **S**



Counter-clockwise **S**

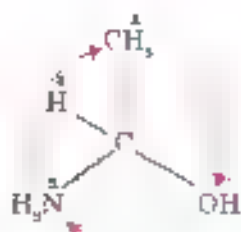
Priority order OH, COOH, CH_3 and H



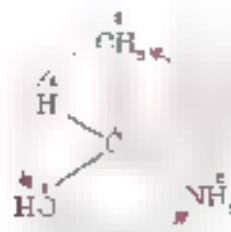
Clockwise, **R**

Competition File

(iii) **1-Amino ethanol** $\text{CH}_3\text{CH}(\text{NH}_2)\text{OH}$ Priority order is $\text{OH} > \text{NH}_2 > \text{CH}_3 > \text{H}$

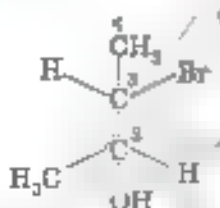


Clockwise **R**

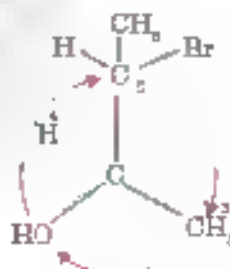
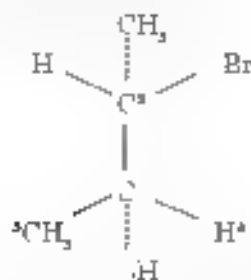


Counter-clockwise **S**

Note : If a molecule contains more than one chiral carbon atom, then the above procedure may be applied to each chiral carbon atom one by one. Let us consider the example of the following isomer of 3-bromobutan-2-ol which contains two chiral carbon atoms 2 and 3.

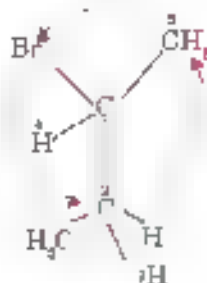
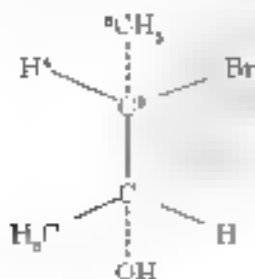


Designation of configuration of C-2. After assigning the priorities, the configuration around C-2 can be predicted as shown below



R

Designation of configuration of C-3



S

The molecule may be represented as (2R, 3S).

Assigning R and S configurations from Fischer Projections

Fischer projections are also helpful to assign R and S configurations. These projections are especially used in case of compounds containing more than one chiral centre. The following steps are followed

Competition File

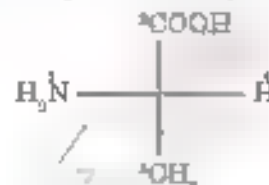
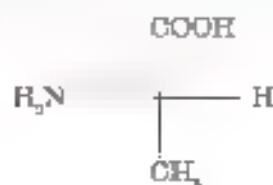
Step 1 Assign priorities to the four substituents in the usual way

Step 2 Perform one of the allowed motions to place the group of lowest priority at the top of the Fischer projection. This means that the lowest priority group is oriented back & away from the viewer as required for assigning configuration.

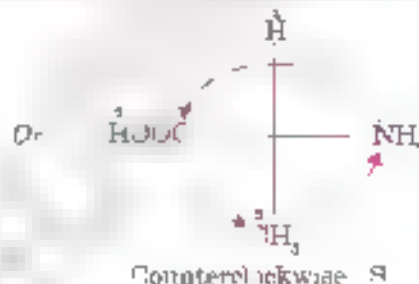
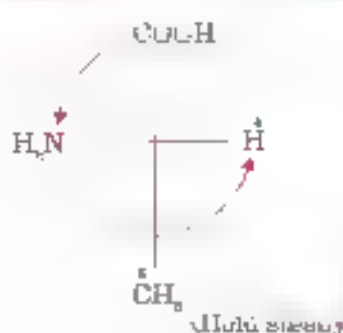
Step 3 Determine the direction of rotation while going from 1 \rightarrow 2 \rightarrow 3 of the remaining three groups and assign R or S.

These steps are explained below

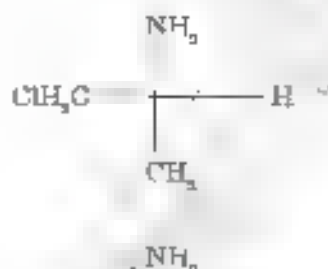
The priority order is NH_2 , COOH , CH_3 and H as



To bring the group of lowest priority (H) to the top, hold the CH_3 group steady and rotate the other three groups and then see the rotation from 1 \rightarrow 2 \rightarrow 3 since it is counter-clockwise the configuration is S.



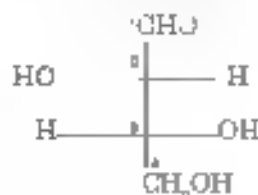
Similarly consider other examples



Priority order NH_2 , CH_2Cl , CH_3 , H

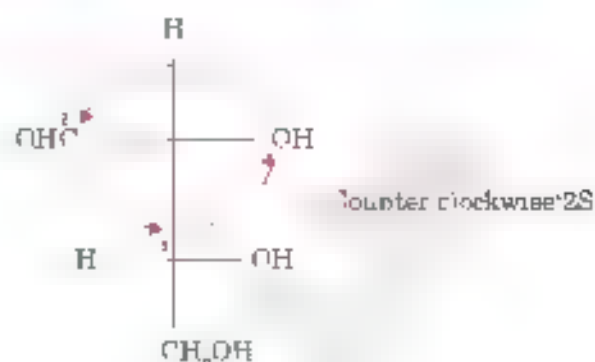
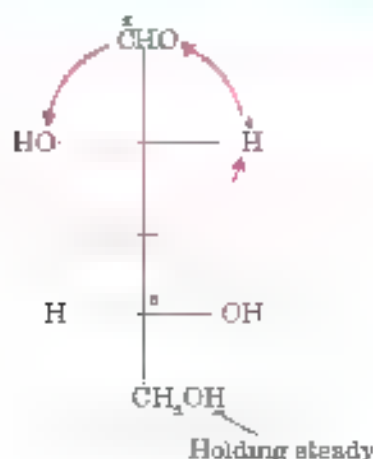


Let us apply to a molecule containing two chiral centres.

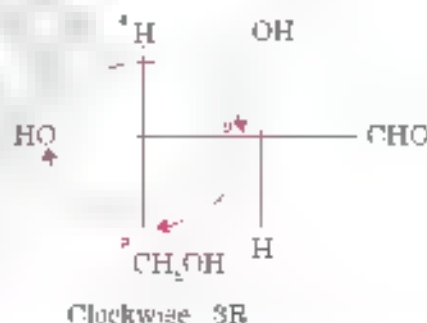
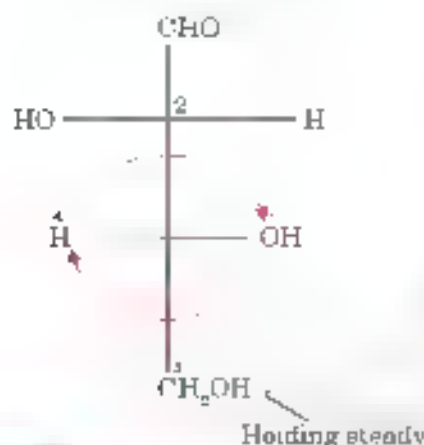


Competition File

Let us assign priorities on C-2. These are -OH, -CHO, C-attached, H



For C-3, priority order is -OH, C attached, CH₂OH and H

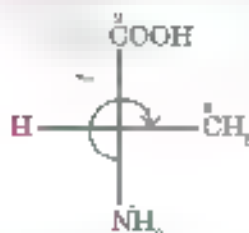


KEY NOTE

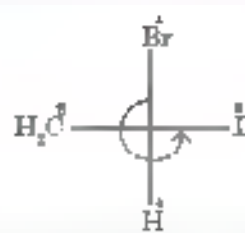
There is a very simple way of predicting the configuration (R or S) from Fischer projection

- Assign priorities to four atoms or groups attached to the chiral centre
- If the atom or group of lowest priority occupies **vertical position (upward or downward)** in the Fischer projection, then the observed configuration is the actual configuration of the molecule.
- If the atom or group of lowest priority occupies **horizontal position (right or left)** in the Fischer projection, then change the observed configuration from R to S or vice versa. This gives the correct configuration.

Illustration

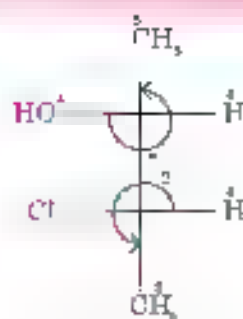


The observed configuration is R.
Since H is on horizontal position, therefore the actual configuration is S.

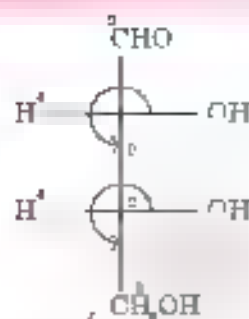


The observed configuration is S.
Since H is on vertical position, therefore the actual configuration is same i.e. S.

Competition File



- S change to R (2R)
(because H is on horizontal position)
- R change to S (3S)
(because H is on horizontal position)

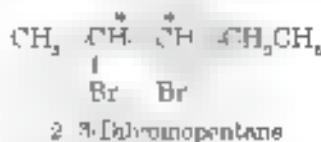


- S change to R (2R)
- S change to S (3S)

► DIASTEREOMERS AND MESO COMPOUNDS

Consider a compound with two different chiral carbon atoms. Each of these two chiral carbons can be either R or S and consequently there are four different ways in which these configurations can be arranged in a molecule. Thus, a molecule with two different chiral carbons can have four stereoisomers. In general, the total number of stereoisomers for a compound is 2^n where n is the number of chiral atoms. If there are two chiral carbons, then there can be upto four ($2^2 = 4$) stereoisomers and when there are three chiral carbon atoms, there can be upto eight ($2^3 = 8$) stereoisomers.

Consider for example a molecule of 2,3-dibromopentane which has two chiral carbon atoms



(C-2 and C-3) Since there are two chiral carbon atoms, we expect four ($2^2 = 4$) stereoisomers. Let us write structure I and its mirror image II



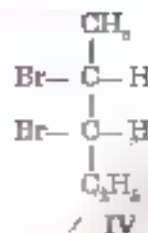
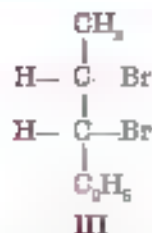
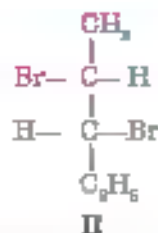
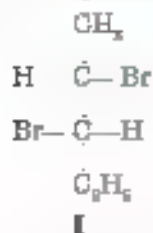
We find that structures I and II are non-super-imposable mirror images. Therefore, these are **enantiomers**. Similarly, we can write structures III and IV. It is clear that structure IV is non-superimposable mirror image of I. Hence, structures III and IV represent another pair of **enantiomers**.



Thus, structures I-IV are all different and therefore, there are in total, **four stereoisomers of 2,3-dibromopentane**.

Competition File

These are given below .



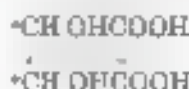
All these compounds are optically active compounds and therefore, are stereoisomers. Any one of these, if placed separately in a polarimeter would show optical activity. The compounds represented by structures I and II are enantiomers and the compounds represented by structures III and IV are enantiomers.

Let us study some relation between structures I and III or between II and III. We observe that I and III or II and III are stereoisomers but are not mirror images of each other. *The stereoisomers which are not mirror images of each other are called diastereomers. Thus, diastereomers are the stereoisomers which are not mirror images of each other.*

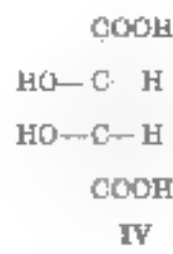
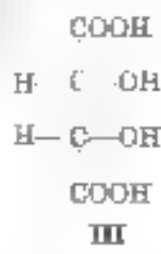
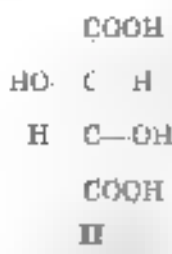
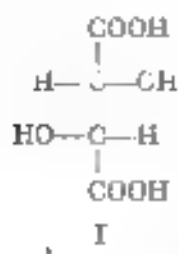
In the above example I and III, II and III and similarly I and IV and II and IV are diastereomers.

Meso Compounds

A molecule with two chiral carbons will not always have four possible stereoisomers. Sometimes, there may be three only. *This is because some molecules with chiral centres are overall achiral.* To understand this, let us consider a tartaric acid molecule which has two asymmetric carbon atoms.



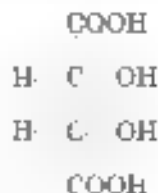
Since there are two asymmetric carbon atoms, we expect four (2^n , n = number of asymmetric C atoms) stereoisomers having the structures, I, II, III and IV as



Enantiomers

Meso-tartaric acid
optically inactive

Structures I and II are non-superimposable mirror image and thus are enantiomers. Structures III and IV are mirror images but one structure can be superimposed on the other. Thus, the molecule is achiral and hence is optically inactive although it contains two asymmetric carbon atoms.



Meso form of tartaric acid

This is called a meso compound. *Thus, meso compound is one whose molecules are superimposable on their mirror images even though they contain chiral centres.*

Thus, meso compounds are optically inactive because they are achiral. In these molecules, there is a plane of symmetry. One-half of the molecule is mirror image of the other half. This molecule is said to have *internal plane of symmetry and hence is achiral*. Thus, tartaric acid exists in three optical isomers.

Competition File

OBJECTIVE TYPE QUESTIONS

Multiple Choice Questions

M. C. Q.

A (Topic-wise) MULTIPLE CHOICE QUESTION with only one correct answe.

Haloalkanes

A1. The IUPAC name of $(\text{CH}_3)_3\text{COI}$ is

- a) 1-chloro-1,1,1-trifluoromethane
b) 1-chloro-2-methylpropane
c) 2-chlorobutane
d) Trimerethylfluoromethane

A2. The IUPAC name of $\text{CH}_3-\text{CH}=\text{CHCH}_2\text{Br}$ is

- a) 1-Bromobut-2-ene b) 1-Bromobut-3-ene
c) 2-Butene-1-bromide d) 4-Bromobut-2-ene

A3. In the reaction



- a) CH_3CHO b) CH_3COI
c) $\text{CH}_3\text{CH}_2\text{OH}$ d) $\text{CH}_3-\text{CH}_2-\text{OH}$

A4. For a given alkyl group, the boiling points of alkyl halides follow the order

- a) $\text{RI} > \text{RBr} > \text{RCl}$ b) $\text{RCl} > \text{RBr} > \text{RI}$
c) $\text{RI} > \text{RCl} > \text{RBr}$ d) $\text{RBr} > \text{RI} > \text{RCl}$

A5. Which of the following is not a chiral?

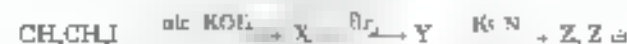
- a) 3-Methylhexane b) 2,3-Dihydroxypropanoic acid
c) 2,3-Dibromobutane d) Butan-2-ol

A6. The reaction



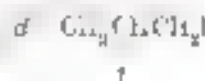
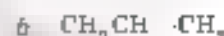
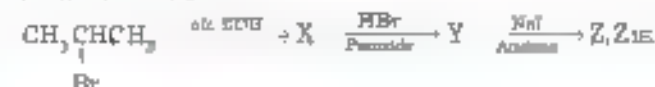
- (a) Sandmeyer's reaction b) Fittig reaction
(c) Wurtz reaction d) Williamson's synthesis.

A7. In the reaction



- a) $\text{CH}_3\text{CH}_2\text{CN}$ b) $\text{CNCH}_2\text{CH}_2\text{CN}$
c) $\text{Br}^-\text{CH}_2\text{CH}_2\text{CN}$ d) $\text{Br}^-\text{CH}=\text{CHCN}$

A8. In the reaction

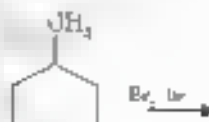


A9. The reagents for the following conversions is/are

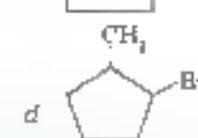
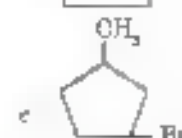
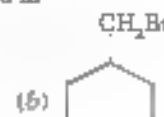
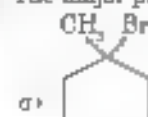


- (a) alcoholic KOH
b) $\text{Zn} | \text{CH}_3\text{OH}$
(c) aq. KOH followed by NaNH_2
(d) alcoholic KOH followed by NaNH_2

A10. In the following reaction



The major product obtained is



A11. In the addition of HBr to propene in the absence of peroxides, the first step involves the addition of

- (a) H^+ (b) Br^+
(c) H^- (d) Br^-

A12. The major product in the reaction is



- a) b)
c) d)

- A1. b A2. a A3. a A4. a A5. c A6. c A7. b A8. a A9. d A10. a
A11. (c) A12. (b)

Competition File

A13. In the reaction,



A and B are respectively

- a) A is $(\text{CH}_3)_3\text{C}=\text{CH}_2$ and B is $(\text{CH}_3)_3\text{COCC}_2\text{H}_5$
 b) A is $(\text{CH}_3)_3\text{COCC}_2\text{H}_5$ and B is $(\text{CH}_3)_3\text{C}=\text{CH}_2$
 c) Both A and B are $(\text{CH}_3)_3\text{C}-\text{CH}_2$
 d) Both A and B are $(\text{CH}_3)_3\text{COCC}_2\text{H}_5$

A14. In $\text{S}_{\text{N}}1$ reaction, the order of reactivity of halides is

- a) $3^\circ > 2^\circ > 1^\circ > \text{methyl}$ b) $\text{methyl} > 1^\circ > 2^\circ > 3^\circ$
 c) $3^\circ > 2^\circ = 1^\circ > \text{methyl}$ d) $2^\circ > 1^\circ > \text{methyl} > 3^\circ$

A15. The product of reaction of alcoholic silver nitrite with ethyl bromide is

- (a) Ethylene (b) Ethyl nitrite
 (c) Nitroethane (d) Ethyl alcohol

A16. C—X bond is strongest in

- (a) CH_3Cl (b) CH_3Br
 (c) CH_3F (d) CH_3I

A17. When ethyl iodide and n-propyl iodide are allowed to react with sodium metal in ether the number of alkanes that could be produced is

- (a) only one (b) two alkanes
 (c) three alkanes (d) four alkanes

A18. 1,3-Dibromopropane reacts with metallic zinc to form

- (a) Propene (b) Propane
 (c) Cyclopropane (d) Hexane

A19. Identify the set of reagents/reaction conditions 'X' and 'Y' in the following set of transformation



- a) X = dilute aqueous solution, $\Delta/0^\circ\text{C}$;
 Y = $\text{HBr}/\text{acetic acid}$ at 20°C
 b) X = dilute aqueous NaOH & C_2
 Y = $\text{HBr}/\text{acetic acid}$ at 20°C
 c) X = dilute aqueous NaOH , 20°C ✓
 Y = $\text{Br}_2/\text{CHCl}_3$, 0°C
 d) X = concentrated alcoholic NaOH , 80°C ;
 Y = Br/CHCl_3 , 0°C

A20. Butane nitrile may be prepared by aceting

- a) propyl alcohol with K^+CN
 b) butyl alcohol with KCN
 c) butyl chloride with KCN
 d) propyl chloride with KCN

A21. Which of the following will be least reactive in nucleophilic substitution?

- a) $\text{CH}_3\text{CH}_2\text{CH}_2\text{Cl}$ b) $\text{CH}_3\text{CH}_2\text{CCl}_3$
 c) $\text{CH}_3=\text{CH}-\text{CH}_2\text{Cl}$ d) $\text{CH}_3=\text{CHCl}$

A22. The reactivity order of halides for dehydrohalogenation is

- a) $\text{R}-\text{F} > \text{R}-\text{Cl} > \text{R}-\text{Br} > \text{R}-\text{I}$
 b) $\text{R}-\text{I} > \text{R}-\text{Br} > \text{R}-\text{Cl} > \text{R}-\text{F}$
 c) $\text{R}-\text{I} > \text{R}-\text{Cl} > \text{R}-\text{Br} > \text{R}-\text{F}$
 d) $\text{R}-\text{F} > \text{R}-\text{I} > \text{R}-\text{Br} > \text{R}-\text{Cl}$

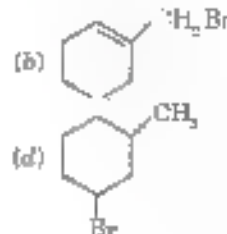
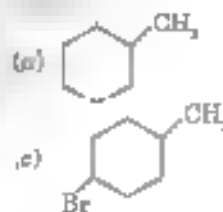
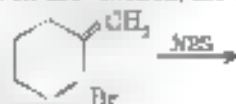
A23. Which one of the following gives only one monochloro derivative?

- a) n-hexane b) 2-methylpentane
 c) 2,4-dimethylpentane d) neo-pentane

A24. The most reactive nucleophile among the following is

- (a) CH_3O^- (b) $\text{C}_2\text{H}_5\text{O}^-$
 (c) $(\text{CH}_3)_2\text{CHO}^-$ (d) $(\text{CH}_3)_3\text{CO}^-$

A25. In the reaction, the major product 'X' is



Haloarenes

A26. Chlorobenzene can be obtained from benzene diazonium chloride by

- a) Gattermann's reaction b) Friedel Crafts reaction
 (c) Wurtz reaction d) Fittig reaction

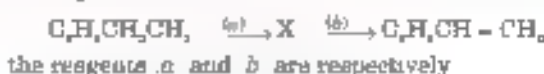
A27. Which of the following is most reactive towards nucleophilic substitution reaction?

- (a) $\text{C}_6\text{H}_5\text{Cl}$ (b) $\text{CH}_2=\text{CHCl}$
 c) $\text{ClCH}_2\text{CH}=\text{CH}_2$ d) $\text{CH}_3\text{CH}=\text{CHCl}$

A28. The reaction of toluene with Cl_2 in the presence of FeCl_3 gives predominantly

- (a) Benzoyl chloride (b) m-chloro toluene
 c) Benzyl chloride d) o- and p-chlorotoluene

A29. During the conversion

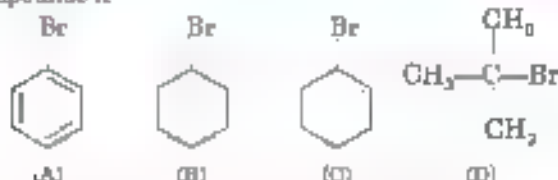


- (a) SOCl_2 & alc KOH (b) Cl_2/hv , H_2O
 c) SO_2Cl_2 & alc KOH (d) SO_2Cl_2 & alc KOH

- A13. b A14. a) A15. c A16. c A17. c A18. c A19. b A20. d) A21. d' A22. b
 A23. d) A24. (a) A25. b) A26. (a) A27. (c) A28. (d) A29. d)

Competition File

A30. The increasing order of hydrolysis of the following compounds is



- a) $A < D < B < C$ b) $A < B < D < C$
 c) $D < C < B < A$ d) $A < B < C < D$

A31. Arrange the following compounds in order of increasing dipole moment

Toluene (I), *m*-dichlorobenzene (II), *p*-dichlorobenzene (III) and *p*-chlorotoluene (IV)

- a) $I < IV < II < III$ b) $IV < I < II < III$
 c) $IV < I < III < II$ d) $IV < II < I < III$

A32. The reaction of $\text{CH}_3\text{CH}=\text{CH}-\text{C}_6\text{H}_4\text{OH}$ with HBr gives

- a) $\text{CH}_3\text{CH}_2\text{CH}_2-\text{C}_6\text{H}_4\text{OH}$
 b) $\text{CH}_3\text{CH}_2\text{CHBr}-\text{C}_6\text{H}_4\text{OH}$
 c) $\text{CH}_3\text{CH}_2\text{CH}_2-\text{C}_6\text{H}_3\text{Br}$
 d) $\text{CH}_3\text{CH}_2\text{CHBr}-\text{C}_6\text{H}_3\text{Br}$

A33. In the following sequence of reactions, B is

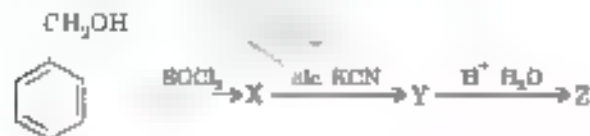


- a) chlorobenzene (b) benzyl chloride
 c) diphenyl (d) chlorophenylmethane

A34. 2-Phenyl-2-chloropropane on treatment with *n*-KOH gives mainly

- a) 2-Phenylpropene (b) 3-Phenylpropene
 c) 1-Phenylpropan-2-ol d) 1-Phenylpropan-3-ol

A35. The major product Z in the following reaction is



- a) Benzamide (b) Benzoic acid
 c) 2-Phenylethanone d) Xylene

A36. Fluorobenzene is prepared by treating benzene diazonium chloride with fluoroboric acid and heating the product obtained. This reaction is known as

- a) Schiemann reaction
 b) Sandmeyer reaction
 c) Gattermann reaction
 d) Ullmann reaction

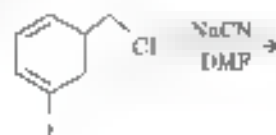
A37. Chlorobenzene is commercially prepared by

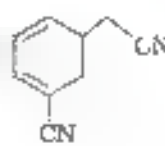
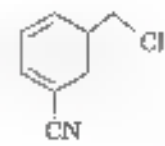
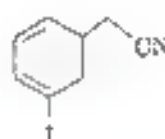
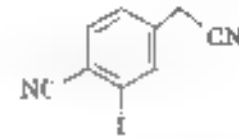
- a) Etard reaction
 b) Wurtz-Fittig reaction
 c) Raschig reaction
 d) Grignard reaction

A38. Chlorobenzene when heated with aqueous ammonia in the presence of Cu_2O under pressure gives

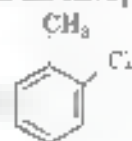
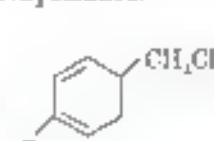
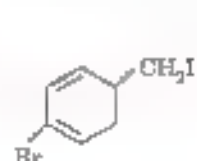
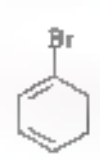
- a) Aniline
 b) Diphenyl
 c) Diphenylamine
 d) Phenyl isocyanide

A39. The structure of the major product formed in the reaction is



- a)  b) 
 c)  d) 

A40. Which of the following will give yellow precipitate on shaking with an aqueous solution of NaOH followed by acidification with dil. HNO_3 and addition of AgNO_3 solution?

- a)  b) 
 c)  d) 

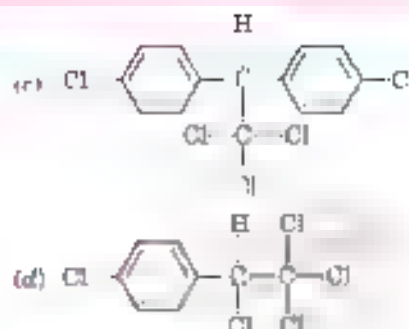
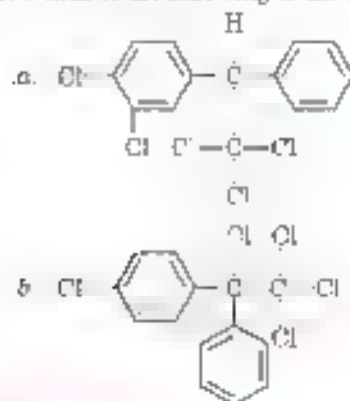
Competition File

Polyhalogenes

A41. Freon-12 is commonly used as

- an insecticide
- a refrigerant
- a solvent
- fire extinguisher

A42. Which of the following is the correct structure of D.D.T?



A43. Benzene hexachloride is used as

- Dye
- Antimalarial drug
- Antibiotic
- Insecticide

A44. When chloroform is exposed to light and damp air it gives among other products

- Carbon tetrachloride
- Carbonyl chloride
- Mustard gas
- Carbon monoxide

A45. D.D.T. is prepared by heating chlorobenzene with

- chloroform
- chloral
- ammonia
- chloropicrin

A41. (b) A42. (c) A43. (d) A44. (b) A45. (b)

B

MULTIPLE CHOICE QUESTIONS

from competitive Examinations

AIJMT & Other State Boards Medical Entrance

B1. For the following

A. I B. Cl C. Br

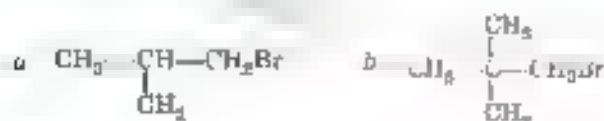
The increasing order of nucleophilicity would be

- Cl < Br < I
- I < Cl < Br
- Br < Cl < I
- I < Br < Cl

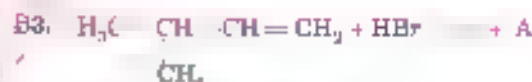
(CBSE Med. 2007)

B2. In a S_N2 substitution reaction of the type

$R-Br + Cl^- \xrightarrow{DMF} R-Cl + Br^-$ which one of the following has the highest reactivity rate

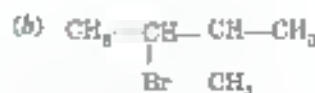
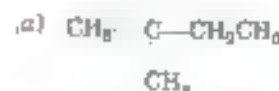


(B.S.E.P.M.T. 2008)



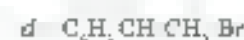
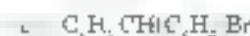
A predominantly is

Br



(C.B.S.E.P.M.T. 2008)

B4. Which one is most reactive towards S_N1 reaction?

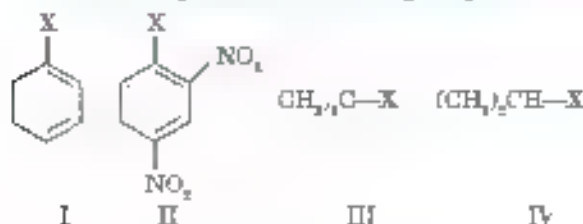


(C.B.S.E.P.M.T. 2010)

B1. (a) B2. (c) B3. (a) B4. (a)

Competition File

B5. The correct order of increasing reactivity of C-X bond towards nucleophile in the following compounds is

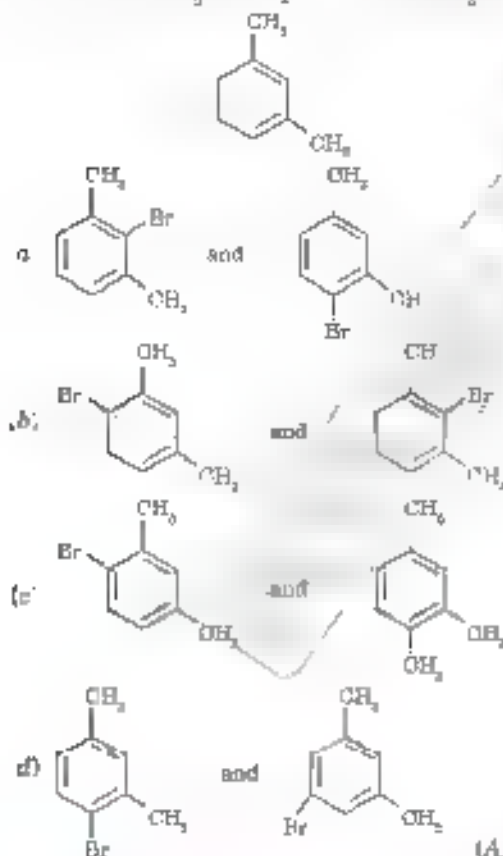


- (c) $I \prec \Pi \prec IV \prec III$ (d) $\Pi \prec III \prec I \prec IV$

86. The reaction of toluene with Cl_2 in the presence of FeCl_3 gives X and the reaction in the presence of light gives Y. Thus, X and Y are

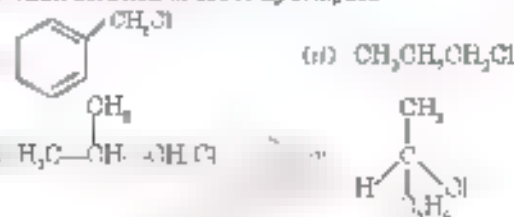
- a) X = benzyl chloride, Y = *m*-chlorotoluene
b) X = benzyl chloride, Y = *p*-chlorotoluene
c) X = *m*-chlorotoluene, Y = *p*-chlorotoluene
d) X = *o*- and *p*-chlorotoluene, Y = trichloromethyl benzene

B7. What products are formed when the following compound is treated with Br_2 in the presence of FeBr_3 ?



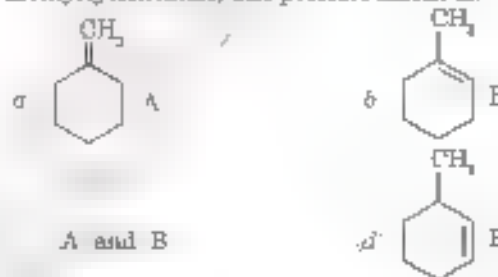
AUGUST 2018

88. Which of the following compounds will undergo racemization when solution of KOH hydrolyzes?



- (c) (iii) and (iv) / (d) (iii) AIPMT 2014

B9. In the reaction with HCl, an alkene reacts in accordance with the Markovnikov's rule, to give a product 1-chloro-1-methylcyclohexane. The possible alkene is,

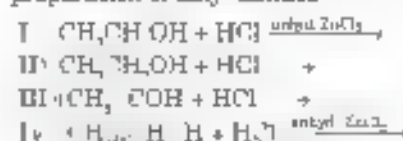


APMT 9015

BIO. In an S₁ reaction on chiral centres, there is

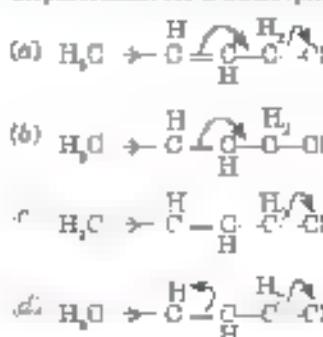
- d) inversion more than retention leading to partial reversion.

B11. Which of the following reactions can be used for the preparation of alkyl halides?



- (c) IV only
(d) I, III, and IV only

B12. Which of the following is the most correct electron displacement for a nucleophilic reaction to take place?



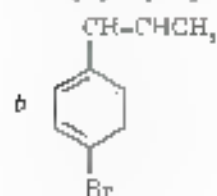
APMT 2015

2020/11/19

- B5. (c)** **B6. (d)** **B7. (c)** **B8. (d)** **B9. (c)** **B10. (d)** **B.1. (c)** **B.2. (a)**

B13. The reaction of $C_6H_5CH=CHCH_3$ with HBr produces

(a) $C_6H_5CH_2CH_2CH_2Br$



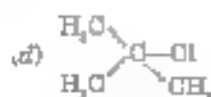
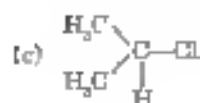
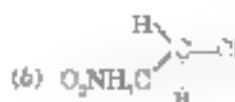
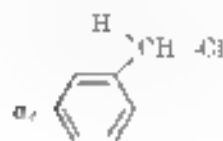
(c) $C_6H_5CHCH_2CH_2Br$

(d) $C_6H_5CH_2CHCH_2Br$

Br

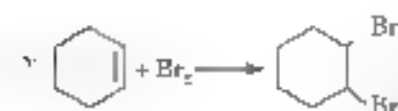
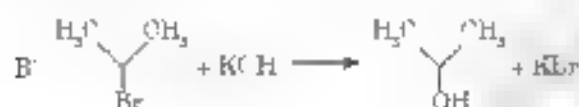
(AIPMT 2015)

B14. In which of the following compounds, the C—Cl bond ionisation shall give most stable carbonium ion?



AIPMT 2015

B15. For the following reactions



Which of the following statement is correct?

- (a) A is elimination, B and C are substitution reactions.
 (b) A is substitution, B and C are addition reactions.
 (c) A and B are elimination reactions and C is addition reaction.
 (d) A is elimination, B is substitution and C is addition reaction.

(NEET 2016)

B16. Consider the reaction:

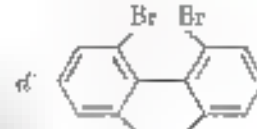
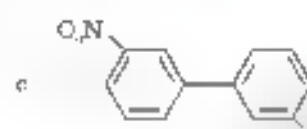
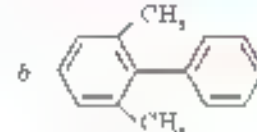
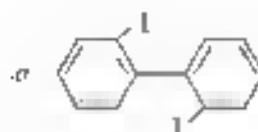


This reaction will be the fastest in

- (a) ethanol
 (b) methanol
 (c) N,N-dimethylformamide (DMF)
 (d) water

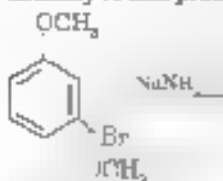
(NEET 2016)

B17. Which of the following biphenyl is optically active?



(NEET 2010)

B18. Identify A and predict the type of reaction.



(a) and elimination addition reaction

(b) and cine substitution reaction

(c) and cine substitution reaction

(d) and substitution reaction

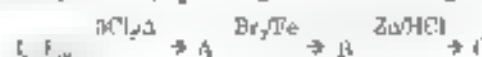
(NEET 2017)

B19. Hydrocarbon (A) reacts with bromine by substitution to form an alkyl bromide which by Wurtz reaction is converted to gaseous hydrocarbon containing less than four carbon atoms. A is

- (a) CH_4
 (b) $CH_2=CH_2$
 (c) CH_3-CH_3
 (d) CH_4

(NEET 2016)

B20. The compound C_6H_5 undergoes the following reactions



The product C is

- (a) m-bromotoluene
 (b) o-bromotoluene
 (c) 3-bromo-5,4-dibromotoluene
 (d) p-bromotoluene

(NEET 2018)

Competition File

B31. The hydrolysis of 2-bromo-3-methylbutane by S_N1 mechanism gives mainly

- (a) 3-methyl-2-butanol (b) 2-methyl-2-butanol
(c) 2,2-dimethyl-2-propanol (d) 2-methyl-1-butanol
(e) 1-pentanol (Kerala P.M.T. 2008)

B32. A dihalogen derivative 'X' of a hydrocarbon with three carbon atoms reacts with alcoholic KOH and produces another hydrocarbon which forms a red precipitate with ammoniacal Cu_2Cl_2 . 'X' gives an aldehyde on reaction with aqueous KOH. The compound 'X' is

- (a) 1,3-Dichloropropane (b) 1,2-Dichloropropane
(c) 2,2-Dichloropropane (d) 1,1-Dichloropropane
(e) 1,3-Dichloropropane (Kerala P.M.T. 2008)

B33. When neopentyl bromide is subjected to Wurtz reaction, the product formed is

- (a) 2,2,4,4-tetramethylhexane
(b) 2,2,4,4-tetramethylpentane
(c) 2,2,5,5-tetramethylhexane
(d) 2,2,3,3-tetramethylhexane
(e) 2,2,3,3-tetramethylpentane (Kerala Med. 2009)

B34. Arrange the following

$CH_3CH_2CH_2Cl$ (I), $CH_3CH_2CHClCH_3$ (II), $CH_3CH(CH_3)CH_2Cl$ (III) and $CH_3CH_2CH_2CH_2Cl$ (IV) in order of decreasing tendency towards S_N2 reactions

- (a) I > III > II > IV (b) II > IV > I > I
(c) II > I > III > IV (d) IV > III > II > I

A.S.I.U. 2011

B35. In alkaline hydrolysis of a tertiary alkyl halide by aqueous alkali, if concentration of alkali is doubled, then the reaction rate at constant temperature

- (a) will be doubled
(b) will be halved
(c) will become four times greater
(d) will be tripled
(e) will remain constant (Kerala P.M.T. 2011)

B36. An alkyl halide with molecular formula $C_6H_{13}Br$ on dehydrohalogenation gave two monomeric alkenes X and Y with molecular formula C_6H_{12} .

On reductive ozonolysis, X and Y gave four compounds CH_3COCH_3 , CH_3CHO , CH_3CH_2CHO and $(CH_3)_2CHCHO$. The alkyl halide is

- (a) 2-bromohexane
(b) 2,2-dimethyl-1-bromopentane
(c) 4-bromo-2-methylpentane
(d) 2-bromo-2,3-dimethylbutane
(e) 3-bromo-2-methylpentane (Kerala P.M.T. 2011)

B37. The compound that does not undergo hydrolysis by S_N1 mechanism is

- (a) CH_3-CHCH_2Cl (b) C_6H_5Cl
(c) $C_6H_5CH_2Cl$ (d) $C_6H_5CH(CH_3)Cl$
(e) $C_6H_5CH(C_6H_5)Cl$ (Kerala P.M.T. 2011)

B38. The major product formed when 2-bromo-2-methylbutane is refluxed with ethanolic KOH is

- (a) 2-methylbut-2-ene (b) 2-methylbutan-1-ol
(c) 3-methylbutan-2-ol (d) 2-methylbutan-2-ol
(e) 2-methylbut-1-ene (Kerala P.M.T. 2014)

B39. The total number of optical isomers possible for 2,3-dibromobutane is

- (a) 2 (b) 4
(c) 0 (d) 3
(e) 8 (Kerala P.M.T. 2015)

B40. Which one of the following organohalogen compounds when heated with alcoholic potassium hydride does not undergo dehydrohalogenation reaction?

- (a) Secondary butyl chloride
(b) Isopropyl chloride
(c) Neopentyl chloride
(d) Isobutyl chloride
(e) Tertiary butyl chloride (Kerala P.M.T. 2015)

JEE (Main) & Other State Boards' Engineering Entrance

B31. $CH_3Br + Nu^- \rightarrow CH_3Nu + Br^-$

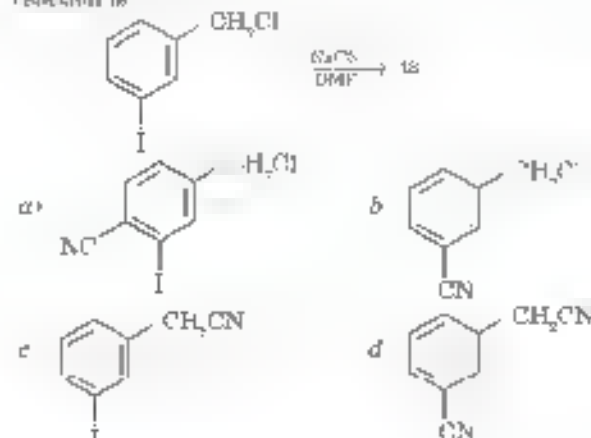
The decreasing order of the rate of the above reaction with nucleophiles Nu^- A to D is

[Nu^- = (A) PhO^- , (B) AcO^- , (C) HO^- , (D) CH_3CO^-]

- (a) D > C > B > A (b) A > B > C > D
(c) B > D > C > A (d) D > C > A > B

A.I.E.E.E. 2006

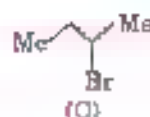
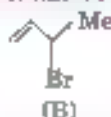
B32. The structure of the major product formed in the following reaction is



A.I.E.E.E. 2006

Competition File

B32. Consider the following bromides:



The correct order of S_N1 reactivity is

- (a) $C > B > A$ (b) $A > B > C$
(c) $B > C > A$ (d) $B > A > C$

(A.I.E.E.E. 2010)

B34. How many chiral compounds are possible on monochlorination of 2-methylbutane?

- (a) 2 (b) 4
(c) 6 (d) 8 (A.I.E.E.E. 2012)

B35. A solution of 1-bromo-1-phenylethane in toluene reacts slowly in the presence of a small amount of $SbCl_5$ due to the formation of

- (a) free radical (b) carbanion
(c) carbene (d) carbocation

(JEE Main 2013)

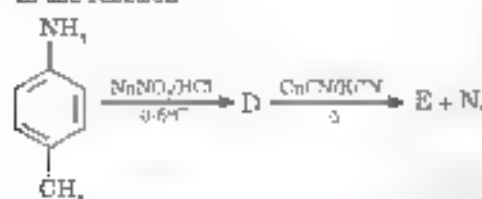
B36. In S_N2 reactions, the correct order of reactivity for the following compounds

CH_3Cl , CH_3CH_2Cl , $(CH_3)_2CHCl$ and CH_3COCl is

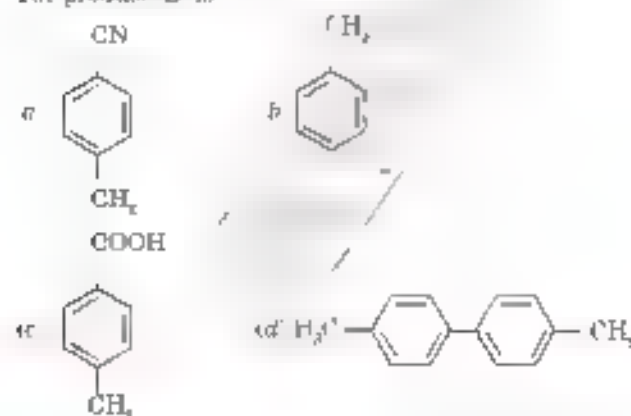
- (a) $(CH_3)_2CHCl > CH_3CH_2Cl > CH_3Cl > (CH_3)_3CCl$
(b) $CH_3Cl > CH_3CH_2Cl > (CH_3)_2CHCl > CH_3COCl$
(c) $CH_3Cl > (CH_3)_2CHCl > CH_3CH_2Cl > CH_3COCl$
(d) $CH_3CH_2Cl > CH_3Cl > CH_3COCl > (CH_3)_2CHCl$

(JEE Main 2014)

B37. In the reaction



The product E is



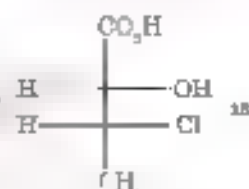
(JEE Main 2015)

B38. The synthesis of alkyl fluorides is best accomplished by

- (a) Finkelstein reaction (b) Swart's reaction
(c) Free radical fluorination (d) Sandmeyer's reaction

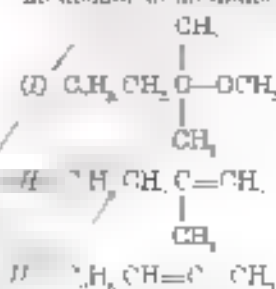
(JEE Main 2010)

B39. The absolute configuration of



- (a) (2R, 3S) (b) (2S, 3R)
(c) (2S, 3S) (d) (2R, 3R) (JEE Main 2016)

B40. 2-Chloro-3-methylpentane on reaction with sodium methoxide in methanol yields



- (a) all of these (b) I and II
(c) III only (d) I and III (JEE Main 2016)

B41. The increasing order of the reactivity of the following halides for the S_N1 reaction is

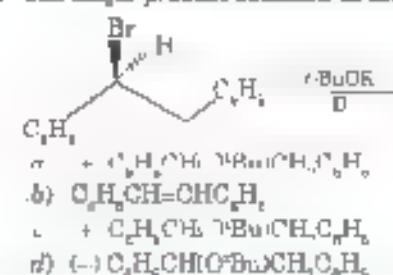
- (I)
- (II)
- (III)
- (a) (III) < (II) < (I) (b) (II) < (I) < (III)
(c) (I) < (II) < (III) (d) (II) < (III) < (I)

(JEE Main 2017)

B42. 3-Methylpent-2-ene on reaction with HBr in presence of peroxide forms an addition product. The number of possible stereoisomers for the product is

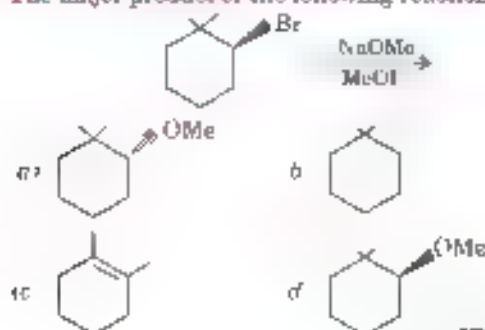
- (a) Six (b) Zero
(c) Two (d) Four (JEE Main 2017)

B43. The major product obtained in the following reaction is



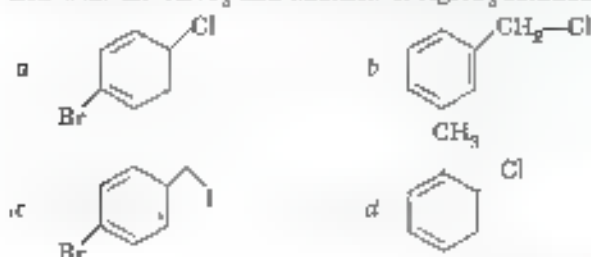
Competition File

B44. The major product of the following reaction is



(JEE Main 2018)

B45. Which of the following will give yellow precipitate on shaking with an aqueous solution of NaOH followed by acidification with dil. HNO_3 and addition of AgNO_3 solution?



(Orissa JEE 2008)

B46. The alkene that will give the same product with HBr in the absence as well as in the presence of peroxide is

- (a) 2-butene (b) 1-butene
 (c) propene (d) 1-hexene
 (e) 2-methylpropene

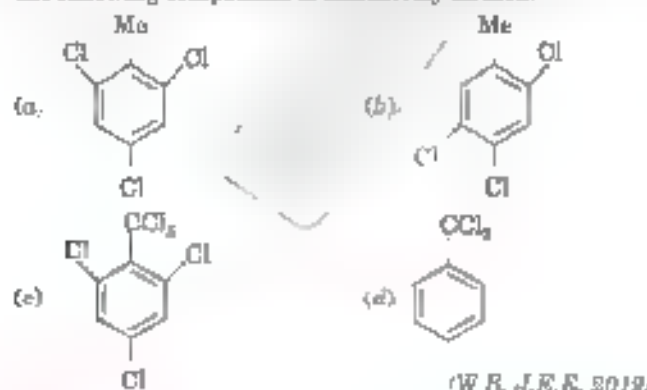
(Kerala PET 2010)

B47. When 3-phenylpropene reacts with HBr in the presence of peroxide, the major product formed is

- (a) 2-bromo-1-phenylpropane
 (b) 1,2-dibromo-3-phenylpropane
 (c) 2-(o-bromophenyl)propene
 (d) 1-bromo-3-phenylpropane

(e) 3-(p-bromophenyl)propene (Kerala PET 2012)

B48. By passing excess of ^{14}C containing CH_3I in benzene, which one of the following compounds is exclusively formed?



(WB JEE 2012)

B49. An alkyl bromide (X) reacts with sodium in ether to form 4,5-diethyloctane. The compound X is

- (a) $\text{CH}_3(\text{CH}_2)_4\text{Br}$
 (b) $\text{CH}_3(\text{CH}_2)_3\text{Br}$
 (c) $\text{CH}_3(\text{CH}_2)_3\text{CH}(\text{Br})\text{CH}_3$
 (d) $\text{CH}_3(\text{CH}_2)_3\text{CH}(\text{Br})\text{CH}_2\text{CH}_3$

(Karnataka CET 2015)

B50. Which of the following pairs are correctly matched?

Reactants	Products
I. $\text{RX} + \text{Ag}(\text{OH})_{\text{alcohol}}$	RH
II. $\text{RX} + \text{AgCN}_{\text{alcohol}}$	RNC
III. $\text{RX} + \text{K}^+\text{N}_{\text{alcohol}}$	RNC
IV. $\text{RX} + \text{Na}_{\text{alcohol}}$	R-R
(a) I alone	(b) I and II
(c) II and III	(d) II and IV

(Karnataka CET 2013)

B51. Which one of the following halogen compounds is difficult to be hydrolysed by $\text{S}_{\text{N}}1$ mechanism?

- (a) Tertiary butyl chloride
 (b) Isopropyl chloride
 (c) Benzyl chloride
 (d) Chlorobenzene

(e) Allyl chloride

(Kerala PET 2018)

B52. How many monochloro structural isomers are expected in free radical monochlorination of 2-methylbutane?

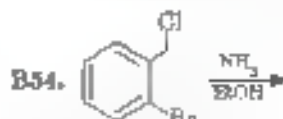
- (a) 2 (b) 3
 (c) 4 (d) 5
 (e) 6

(Kerala PET 2014)

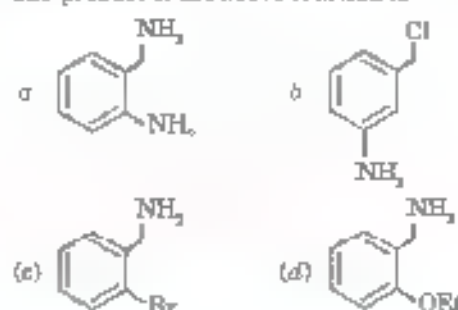
B53. The hydrolysis of optically active 2-bromobutane with aqueous NaOH results in the formation of

- (a) (+)-butan-2-ol (b) (+)-butan-2-ol
 (c) (+)-butan-2-ol (d) (+)-butan-2-ol

(Karnataka CET 2016)



The product of the above reaction is



(WB JEE 2016)

10130/12

Competition File

B55. The compound which is not formed when a mixture of *n*-butyl bromide and ethyl bromide treated with sodium metal in presence of dry ether is:

- (a) Butane (b) Octane
(c) Hexane (d) Ethane *MH-CET 2016*

B56. The total number of monohalogenated products formed by halogenation of 2, 4, 4-trimethylhexane is

- (a) 5 (b) 7
(c) 8 (d) 8

Kerala PET 2016

B57. The major product obtained by the addition reaction of HBr to 4-methylpent-1-ene in the presence of peroxide is

- (a) 1-bromo-4-methylpentane
(b) 4-bromo-2-methylpentane
(c) 3-bromo-4-methylpentane
(d) 3-bromo-2-methylpentane
(e) 2-bromo-2-methylpentane

Kerala PET 2016

B58. Replacement of Cl of chlorobenzene to give phenol requires drastic conditions, but Cl of 2, 4-dinitrochlorobenzene is readily replaced. This is because

- (a) NO_2 group makes the ring electron rich at *ortho* and *para* positions
(b) NO_2 group withdraws electrons from *meta* position
(c) NO_2 donates electrons at *meta* position
(d) NO_2 withdraws electrons from *ortho* and *para* positions

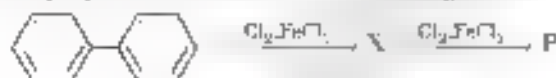
Karnataka CET 2010

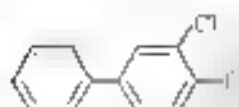


B59. Toluene reacts with halogen in presence of iron (III) chloride giving *ortho*- and *para*- halo compounds. The reaction is

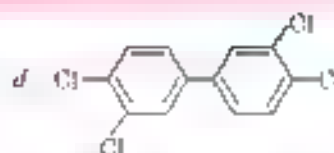
- (a) free radical addition reaction
(b) electrophilic elimination reaction
(c) nucleophilic substitution reaction
(d) electrophilic substitution reaction

Karnataka CET 2017

B60. The major product P formed in the following reaction is



- (a) 
(b) 
(c) 



Kerala PET 2018

B61. The correct order of increasing reactivity of the following alkyl halides CH_3Cl , CH_3Br , CH_3I , $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{Br}$, $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{I}$ and $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{Br}$ towards $\text{S}_\text{N}2$ displacement is

- (a) $\text{I} < \text{II} < \text{III} < \text{IV}$ (b) $\text{III} < \text{I} < \text{IV} < \text{II}$
(c) $\text{III} < \text{I} < \text{II} < \text{IV}$ (d) $\text{II} < \text{IV} < \text{I} < \text{III}$
(e) $\text{I} < \text{III} < \text{II} < \text{IV}$

Kerala PET 2017

B62. Which of the following statement is true in case of alkyl halides?

- (a) They are polar in nature.
(b) They can form hydrogen bonds
(c) They are highly soluble in water
(d) They undergo addition reactions

Karnataka CET 2018

B63. *n*-Propyl chloride reacts with sodium metal in dry ether to give

- (a) $\text{CH}_3\text{—CH}_2\text{—CH}_2\text{—CH}_2\text{—CH}_2\text{—CH}_3$
(b) $\text{CH}_3\text{—CH}_2\text{—CH}_3$
(c) $\text{CH}_3\text{—CH}_2\text{—CH}_2\text{—OH}$
(d) $\text{CH}_3\text{—CH}_2\text{—CH}_2\text{—CH}_2\text{—CH}_2\text{—CH}_3$

Karnataka CET 2018

B64. Tertiary alkyl halide is practically inert to substitution by $\text{S}_\text{N}2$ mechanism because of

- (a) insolubility (b) instability
(c) inductive effect (d) steric hindrance

Karnataka CET 2018

B65. Neopentyl bromide undergoes dehydrohalogenation to give alkenes even though it has no β -hydrogen. This is due to

- (a) Ei mechanism
(b) E_1 mechanism
(c) rearrangement of carbocations by Ei mechanism
(d) E1CB mechanism
(e) E1 mechanism

Kerala PET 2018

B66. The compound which does not lead to nitrile by substitution with NaCN/DMSO is

- (a) benzyl chloride (b) ethyl chloride
(c) iso-propyl chloride (d) chlorobenzene
(e) iso-butyl chloride

Kerala PET 2018

- B55. (d) B56. (c) B57. (a) B58. (d) B59. (d) B60. (b) B61. (b) B62. (a) B63. (a) B64. (d)
B65. (c) B66. (d)

Competition File

B67. The number of possible organobromine compounds which can be obtained in the allylic bromination of 1-butene with *N*-bromosuccinimide is

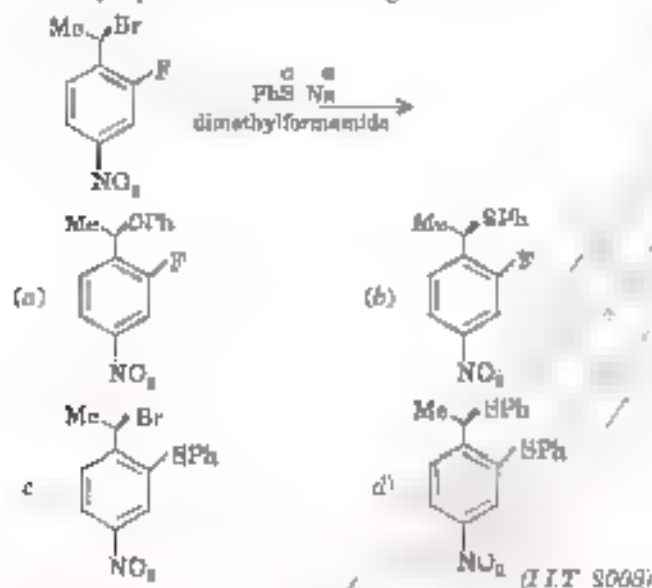
- (a) 1 (b) 2
(c) 3 (d) 4 WB JEE, 2018

JEE Advance) for IIT Entrance

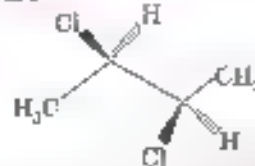
B68. What would be the product formed when 1-bromo-3-chloro cyclobutane reacts with two equivalents of metallic sodium in ether?



B69. The major product of the following reaction is



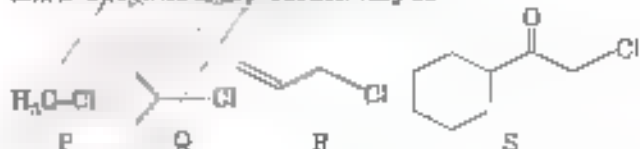
B70. The correct statement(s) about the compound given below is/are



- (a) The compound is optically active
(b) The compound possesses centre of symmetry
(c) The compound possesses plane of symmetry
(d) The compound possesses axis of symmetry

IIT 2008

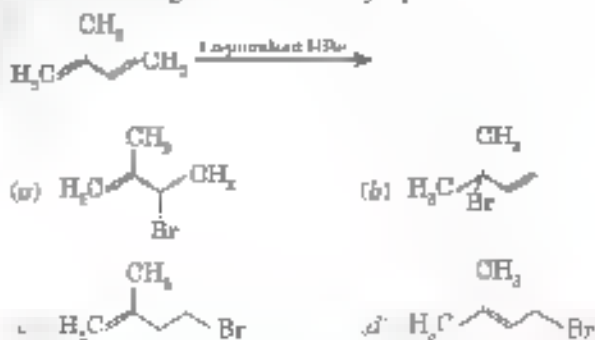
B71. KI in acetone, undergoes S_N2 reaction with each of P, Q, R and S. The rates of the reaction vary as



- (a) $P > Q > R > S$ (b) $S > P > R > Q$
(c) $P > R > Q > S$ (d) $R > P > S > Q$

(JEE Advance 2018)

B72. In the following reaction, the major product is



(JEE Advance 2015)

B67. (d) B68. (d) B69. (a) B70. (a) B71. (b) B72. (d)

C (MULTIPLE CHOICE QUESTIONS with more than one correct answers

C1. Dipole moment is shown by

- (a) Benzoyl chloride
(b) *cis*-1,2-dichloroethene
(c) *trans*-1,2-dichloroethene
(d) *trans*-1,2-dichloropent-2-ene

C2. Aryl halides are less reactive towards nucleophilic substitution reaction than alkyl halides due to

- (a) the formation of less stable carbonium ion
(b) resonance stabilization
(c) longer carbon-halogen bond
(d) sp^2 -hybridised carbon attached to halogen

C1. a, b, d C2. b, d

Competition File

C3. In the reaction



- (a) Pentane-2-one (b) Acetophenone
(c) Hexane-2,5-dione (d) 4-keto pentanoic acid

C4. Benzyl chloride can be prepared from toluene by chlorination with

- (a) SO_2Cl_2 (b) $SOCl_2$
(c) $Cl_2, h\nu$ (d) $NaOCl$

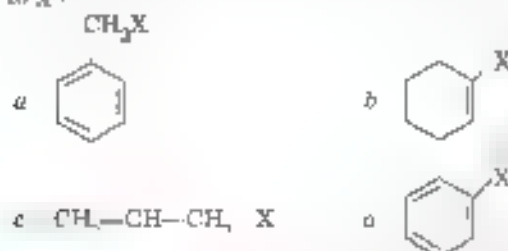
C5. A new carbon-carbon bond formation is possible in the following reaction/reactions

- (a) $C_6H_6 + CH_3Cl \xrightarrow{AlCl_3}$
(b) $CH_3CH_2Br + CH_3CH_2NH_2 \rightarrow$
(c) $CH_3CH_2Br + Na^+ OCH_3 \rightarrow$
(d) $CH_3CH_2Br + KCN(alc.) \rightarrow$

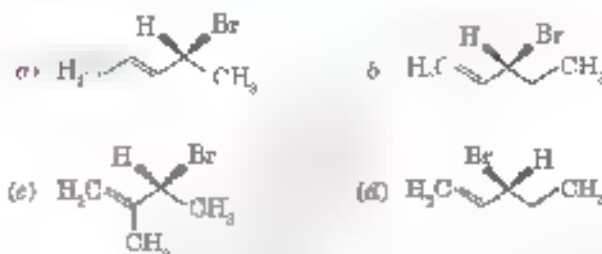
C6. Which of the following statements are correct?

- (a) Benzyl halides are more reactive than vinyl and aryl halides
(b) Vinyl halides are more reactive than alkyl halides
(c) Aryl halides are less reactive than alkyl halides
(d) Aryl halides are more reactive than benzyl halides

C7. Which of the following contains sp^2 hybridised carbon bonded to X?



C8. Compound(s) that on hydrogenation produce(s) optically inactive compound(s) is/are)



JEE Advance 2016

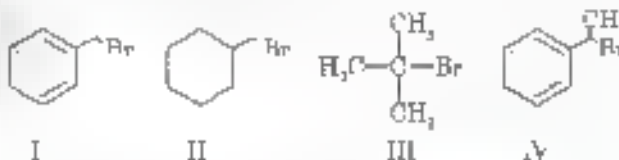
C9. The IUPAC name(s) of the following compound is/are



- (a) 1-chloro-4-methylbenzene
(b) 4-chlorotoluene
(c) 1-methyl-4-chlorobenzene
(d) 4-methylchlorobenzene.

JEE Advance 2017

C10. For the following compounds, the correct statement(s) with respect to nucleophilic substitution reactions is/are



- (a) I and II follow S_N2 mechanism
(b) compound IV undergoes inversion of configuration
(c) the order of reactivity for I, III, and IV is $IV > I > III$
(d) I and III follow S_N1 mechanism.

JEE Advance 2017

- C3. c, d C4. a, c C5. c, d C6. b, c C7. b, d C8. b, d C9. a, b C10. a, b, d

D (MULTIPLE CHOICE QUESTIONS

based on the given passage/comprehension

Passage 1.

Alkyl halides undergo nucleophilic substitution reactions in which halogen atom is replaced by other atom



These reactions follow S_N1 and S_N2 type mechanism in which S_N1 takes place in two steps while S_N2 takes place in single step. Due to their tendency to undergo substitution by a large number of nucleophiles, they form a variety of products.

Answer the following questions

D1. In which of the following pairs, the first nucleophile is stronger?

- (a) Cl^- , I^-
(b) CH_3OH , CH_3S^-
(c) $(CH_3CH_2)_3NH$, $(CH_3CH_2)_3N$
(d) $C_6H_5O^-$, C_6H_5N

D2. Which of the following is least reactive towards S_N2 mechanism?

- (a) $CH_3CH_2CH_2CH_2Br$ (b) $CH_3CH_2C(CH_3)_2Br$
(c) CH_3CH_2Br (d) $(CH_3)_3CHBr$

Answers

Passage I D1. c D2. b

Competition File

D3. In which of the following pairs, the first compound is better S_N2 substrate?

- (a) 1-bromo-1-methyl cyclohexane, cyclohexyl bromide
 (b) 1-iodo-2, 2-dimethyl propane, isopropyl iodide
 (c) 2, 2-dimethyl-1-chlorobutane, 2-chlorobutane
 (d) isopropyl bromide, 2-bromobutane

D4. In which of the following nucleophilic substitution reaction, the product formed is racemic mixture?

- (a) $(CH_3)_3CBr$ (b) CH_3CH_2Br
 (c) $(CH_3CH_2)_2CHBr$ (d) $C_4H_9CH_2Br$

D5. Which of the following has highest nucleophilicity?

- (a) SH^- (b) H_2O
 (c) OH^- (d) F^-

Passage II.

A chlorocompound (A, on reduction with Zn-Cu and ethanol gives the hydrocarbon B) with five carbon atoms. When A is dissolved in dry ether and treated with sodium metal it gave 2,2,5,5-tetra methyl hexane. The treatment of A as



Answer the following questions

D6. The compound A is

- (a) 1-chloro-2, 2-dimethyl propane
 (b) 1-chloro-2, 2-dimethyl butane
 (c) 1-chloro-2-methyl butane
 (d) 2-chloro-2-methyl butane

D7. The reaction of C with Na, C_2H_5OH gives

- (a) $(CH_3)_2C=CHCONH_2$
 (b) $(CH_3)_2C=NH_2$
 (c) $(CH_3)_2C=CHNH_2$
 (d) $(CH_3)_2CHCH=NH_2$

D8. The reaction of C with Na, C_2H_5OH is called

- (a) Gilman reaction
 (b) Madella reaction
 (c) Grignard process
 (d) Swart's reaction

D9. The reaction of A with aq. KOH will preferably favour

- (a) S_N1 mechanism (b) S_N2 mechanism
 (c) E_1 mechanism (d) E_2 mechanism

D3. (d) D4. (a) D5. (a) Passage II D6. (a) D7. (c) D8. (b) D9. (a)

Assertion Reason Type Questions

The question given below consist of an Assertion and the Reason. Use the following key to choose the appropriate answer

- a. If both assertion and reason are CORRECT and reason is the correct explanation of the assertion.
 b. If both assertion and reason are CORRECT but reason is NOT THE CORRECT explanation of the assertion.
 c. If assertion is CORRECT but reason is INCORRECT
 d. If assertion is INCORRECT but reason is CORRECT
 e. If both assertion and reason are INCORRECT

1. Assertion: Addition of Br_2 to but-1-ene gives two optical isomers.

Reason : The product contains one asymmetric carbon atom.

2. Assertion: S_N2 reaction proceeds with inversion of configuration

Reason : S_N2 reactions occur in one step.

3. Assertion: Addition of Br_2 to trans-2-butene yields meso-2,3-dibromobutane

Reason : Bromine addition to an alkene is an electrophilic addition reaction. (I. T. 2001)

4. Assertion: Benzyl bromide when kept in acetone-water, it produces benzyl alcohol

Reason : The reaction follows S_N2 mechanism.

AIIMS 2008

5. Assertion: The nucleophilic substitution of vinyl chloride is difficult than ethyl chloride.

Reason : Vinyl group is electron donating group

6. Assertion: tert-butyl bromide undergoes S_N1 nucleophilic substitution readily than n-butyl bromide.

Reason : It proceeds by the formation of stable carbocation

7. Assertion: Ethanol gives iodoform test while methanol does not.

Reason : Ethanol is less reactive than methanol towards nucleophilic addition reactions.

8. Assertion: Treatment of chloroethane with a saturated solution of $AgCN$ give ethyl isocyanide as the major product

Reason : Cyanide ion (CN^-) is an ambident nucleophile.

(AIIMS 2014)

9. Assertion: 2-Bromobutane on reaction with sodium methoxide in ethanol gives 1-butene as the major product

Reason : 1-But-1-ene is more stable than 2-but-2-ene

AIIMS 2004

10. Assertion: Alkyl iodide can be prepared by treating alkyl chloride/bromide with NaI in acetone

Reason : $NaCl$ and $NaBr$ are soluble in acetone but NaI is not. (AIIMS 2007)

ANSWERS

1. (a), 2. (b), 3. (b), 4. (c), 5. (c), 6. (a), 7. (b), 8. (b), 9. (a), 10. (c)

Competition File

Integer Type Questions

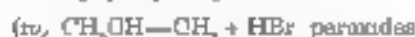
The answer to each of the following question is a **single-digit-integer** ranging from 0 to 9.

1. The number of compounds showing enantiomers among the following compounds is

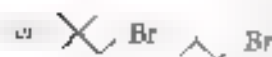
Butan-2-ol, 4-Hydroxypropanoic acid, 2-Methylhexane, 2-Chlorobutane, 2-Bromo-2-chlorobutane.

2-Methylbutanoic acid, isopropyl chloride

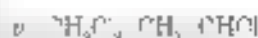
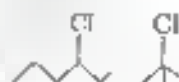
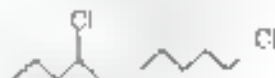
2. The number of reactions proceeding through free radical mechanism are



3. In how many pairs the first compound reacts faster than the second in S_N2 reaction with OH^- ?



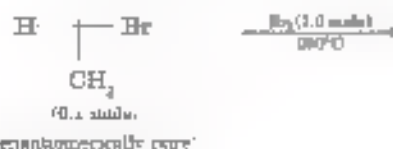
4. In how many pairs, the second compound reacts faster than the first in S_N2 reaction with OH^- ?



5. The number of isomers having the molecular formula $C_4H_{11}Br$ is

6. The total number of alkenes possible by dehydrobromination of 2-bromocyclopentylhexane using alcoholic KOH is

7. In the following monobromination reaction, the number of possible chiral products is



Competition File

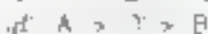
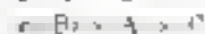
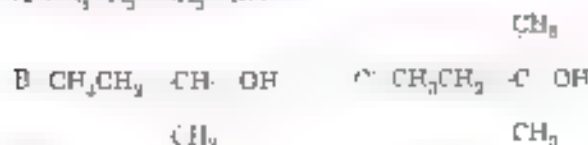
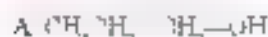


NCERT

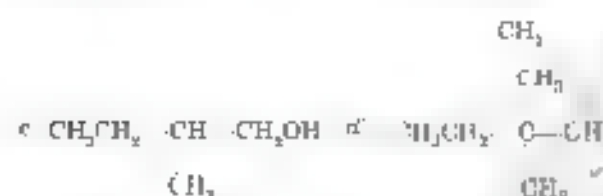
Exemplar Problems
Objective Questions

Multiple Choice Questions (Type-I)

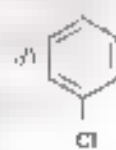
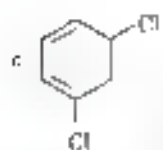
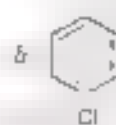
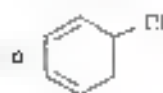
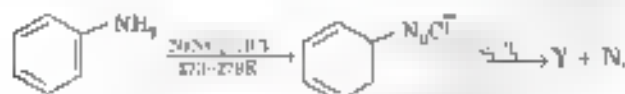
1. The order of reactivity of following alcohols with halogen acids is



2. Which of the following alcohols will yield the corresponding acyl chloride on reaction with concentrated HCl at room temperature?



3. Identify the compound Y in the following reaction.

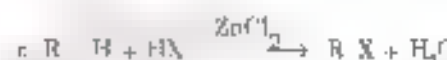
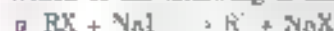


4. Toluene reacts with a halogen in the presence of iron chloride giving *ortho* and *para* halo compounds. The reaction is

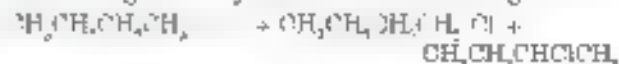
- a Electrophilic elimination reaction
b Electrophilic substitution reaction

- c Free radical addition reaction
d Nucleophilic substitution reaction

5. Which of the following is halogen exchange reaction?

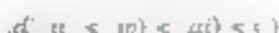
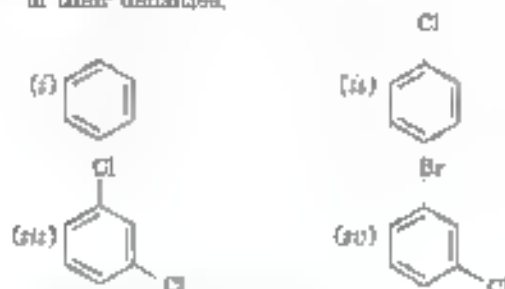


6. Which reagent will give rise for the following reaction?



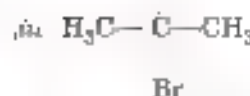
- a Cl_2 / UV light
b $\text{NaCl} + \text{H}_2\text{SO}_4$
c Cl_2 gas in dark
d Cl_2 gas in the presence of iron in dark

7. Arrange the following compounds in the increasing order of their densities.



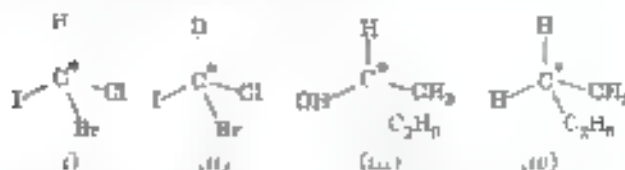
Competition File

8. Arrange the following compounds in increasing order of their boiling points



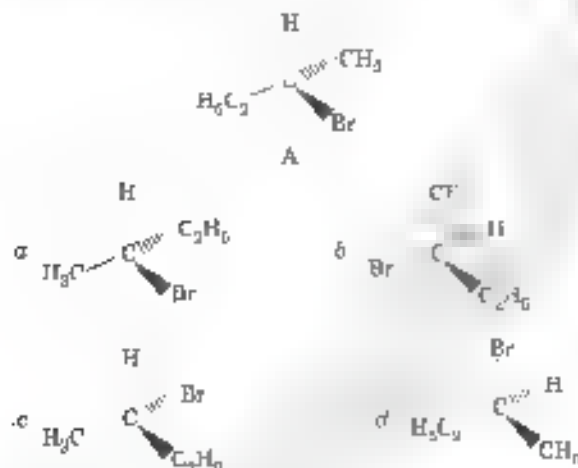
- a. $ii < (i) < iii$ b. $i < ii < iii$
 c. $iii < (i) < ii$ d. $iii < i < ii$

9. In which of the following molecules carbon atom marked with asterisk (*) is asymmetric?



- a. (i), (ii), (iii), (iv) b. (i), (ii), (iii)
 c. (ii), (iii), (iv) d. (i), (iii), (iv)

10. Which of the following structures is enantiomeric with the molecule A) given below?



11. Which of the following is an example of vic-dihalide?

- a. Dichloromethane b. 1,2-dichloroethane
 c. Ethylene chloride d. Allyl chloride

12. The position of Br in the compound in $\text{CH}_3\text{CH}=\text{CHC}(\text{Br})(\text{CH}_3)_2$ can be classified as

- a. Allyl b. Aryl
 c. Vinylic d. Secondary

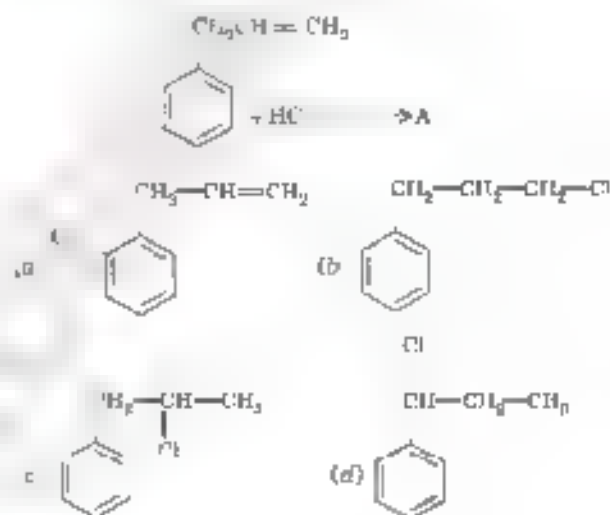
13. Chlorobenzene is formed by reaction of chlorine with benzene in the presence of AlCl_3 . Which of the following species attacks the benzene ring in this reaction?

- a. Cl^\cdot b. Cl_2
 c. AlCl_3 d. $[\text{AlCl}_4]^\cdot$

14. Ethylidene chloride is a/an

- a. vic-dihalide b. gem-dihalide
 c. allylic halide d. vinylic halide

15. What is A in the following reaction?



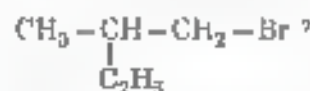
16. A primary alkyl halide would prefer to undergo

- a. $\text{S}_{\text{N}}1$ reaction b. $\text{S}_{\text{N}}2$ reaction
 c. E1 elimination d. Racemisation

17. Which of the following alkyl halides will undergo $\text{S}_{\text{N}}1$ reaction most readily?

- a. $(\text{CH}_3)_3\text{C}-\text{F}$ b. $(\text{CH}_3)_3\text{C}-\text{Cl}$
 c. $(\text{CH}_3)_3\text{C}-\text{Br}$ d. $(\text{CH}_3)_3\text{C}-\text{I}$

18. Which is the correct IUPAC name for



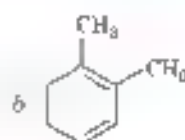
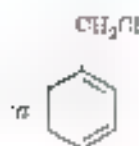
- a. 1-Bromo-2-ethylpropane
 b. 1-Bromo-2-ethyl-2-methylpropane
 c. 1-Bromo-2-methylbutane
 d. 2-Methyl-1-bromobutane

19. What should be the correct IUPAC name for diethylbromomethane?

- a. 1-Bromo-1,1-diethylmethane b. 3-Bromopentane
 c. 1-Bromo-1-ethylpropane d. 1-Bromopentane

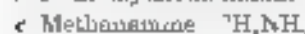
Competition File

30. The reaction of toluene with chlorine in the presence of iron and in the absence of light yields



d Mixture of a and c

31. Chloromethane on treatment with excess of ammonia yields mainly



d Mixture containing all these in equal proportion

32. Molecules whose mirror image is non superimposable over them are known as chiral. Which of the following molecules is chiral in nature?



33. Reaction of $\text{C}_6\text{H}_5\text{CH}_2\text{Br}$ with aqueous sodium hydride follows

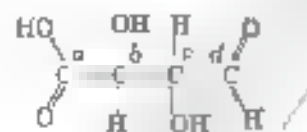
a $\text{S}_{\text{N}}1$ mechanism

b $\text{S}_{\text{N}}2$ mechanism

c Any of the above two depending upon the temperature of reaction

d Saytzeff rule

34. Which of the carbon atoms present in the molecule given below are asymmetric?



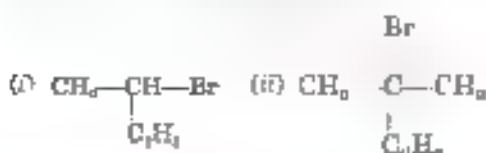
a a, b, c, d

(c) a, d

b. b, c

(d) a, b, c

35. Which of the following compounds will give racemic mixture on nucleophilic substitution by OH^- ion?



a) (i)

(c) (iii), (iv)

b) (i), (iii), (iv)

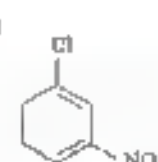
d) (i), (iv)

Note : In the questions 26 to 29 arrange the compounds in increasing order of rate of reaction towards nucleophilic substitution.

26. (i)



(iii)



a) $(i) < (ii) < (iii)$

(c) $(iii) < (i) < (ii)$

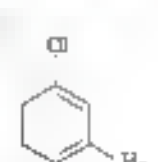
b) $(i) < (iii) < (ii)$

d) $(iii) < (ii) < (i)$

27. (i)



(iii)



a) $(i) < (ii) < (iii)$

(c) $(iii) < (i) < (ii)$

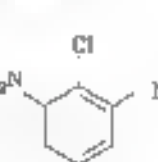
b) $(i) < (iii) < (ii)$

d) $(iii) < (ii) < (i)$

28. (i)



(iii)



(a) $(iii) < (ii) < (i)$

(c) $(i) < (ii) < (iii)$

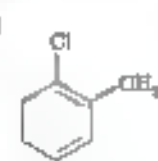
(b) $(i) < (iii) < (ii)$

d) $(ii) < (i) < (iii)$

29. (i)



(iii)



(a) $(i) < (iii) < (ii)$

(c) $(iii) < (ii) < (i)$

(b) $(i) < (ii) < (iii)$

d) $(i) < (iii) < (ii)$

Competition File

30. Which is the correct increasing order of boiling points of the following compounds ?

- a) Iodobutane, 1-Bromobutane, 1-Chlorobutane, Butane
 b) Butane < 1-Iodobutane < 1-Bromobutane < 1-Chlorobutane
 c) Butane < 1-Iodobutane < 1-Bromobutane < 1-Chlorobutane
 d) Butane < 1-Chlorobutane < 1-Iodobutane < 1-Bromobutane

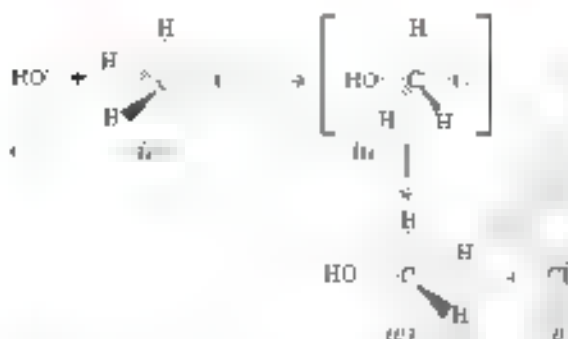
31. Which is the correct increasing order of boiling points of the following compounds ?

- 1-Bromoethane, 1-Bromopropane, 1-Bromobutane, Bromobenzene
 a) Bromobenzene < 1-Bromobutane < 1-Bromopropane < 1-Bromoethane
 b) Bromobenzene < 1-Bromoethane < 1-Bromopropane < 1-Bromobutane
 c) 1-Bromopropane < Bromobenzene < 1-Bromoethane < 1-Bromobutane
 d) 1-Bromoethane < 1-Bromopropane < 1-Bromobutane < Bromobenzene

30. (a), 31. (d)

▶▶ Reaction of Hydroxide Ion with (R)-2-Chlorobutane ▶▶

Note : In the following questions two or more options may be correct. Consider the following reaction and answer the questions no. 32–34



32. Which of the statements are correct about above reaction ?

- a) (i) and (v) both are nucleophiles.
 b) In (iii) carbon atom is sp^3 hybridised.
 c) In (iv) carbon atom is sp^2 hybridised.
 d) (i) and (v) both are electrophiles.

33. Which of the following statements are correct about this reaction ?

- a) The given reaction follows S_N2 mechanism.
 b) (i) and (iv) have opposite configuration.
 c) (ii) and (iv) have same configuration.
 d) The given reaction follows S_N1 mechanism.

34. Which of the following statements are correct about the reaction intermediate ?

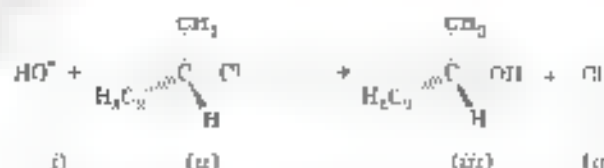
- a) Intermediate (ii) is unstable because in this carbon is attached to 5 atoms.

b) Intermediate (ii) is unstable because carbon atom is sp hybridised.

c) Intermediate (iii) is stable because carbon atom is sp^2 hybridised.

d) Intermediate (iv) is less stable than the reactant (i).

Answer Q. Nos. 35 and 36 on the basis of the following reaction.



35. Which of the following statements are correct about the mechanism of this reaction ?

- a) A carbocation will be formed as an intermediate in the reaction.
 b) OH^- will attack the substrate (i) from one side and Cl^- will leave it simultaneously from other side.
 c) An unstable intermediate will be formed in which OH^- and Cl^- will be attached by weak bonds.
 d) Reaction proceeds through S_N1 mechanism.

36. Which of the following statements are correct about the kinetics of this reaction ?

- a) The rate of reaction depends on the concentration of only (i).
 b) The rate of reaction depends on concentration of both (i) and (ii).
 c) Molecularity of reaction is one.
 d) Molecularity of reaction is two.

Answers

32. (a), (c)

33. (a), (b)

34. (a), (d)

35. (a), (d)

36. (a), (c)

Competition File

37. Halonalkanes contain halogen atom (x) attached to the sp^3 hybridised carbon atom of an alkyl group. Identify halonalkanes from the following compounds
- 2-Bromononane
 - Vinyl chloride (chloromethene)
 - 2-chlorooctanone
 - Trichloroethane
38. Ethylene chloride and ethyldene chloride are isomers. Identify the correct statements.
- Both the compounds form same product on treatment with alcoholic KOH
 - Both the compounds form same product on treatment with aq. $NaOH$
 - Both the compounds form same product on reduction.
 - Both the compounds are optically active
39. Which of the following compounds are gem-dihalides?
- Ethyldene chloride
 - Ethylene dichloride
 - Methylene chloride
 - Benzyl chloride
40. Which of the following are secondary bromides?
- H_3C-CH_2Br
 - $(CH_3)_2CHBr$
 - CH_3-CH_2Br
 - $CH_3-CHBr-CH_3$
41. Which of the following compounds can be classified as aryl halides?
- $p-Cl-C_6H_4-CH_2CH_2OH$
 - $p-Cl-C_6H_4-CH_2CH_2CH_3$
 - $o-Br-C_6H_4-CH_2CH_2-CH_2CH_2CH_3$
 - C_6H_5-Cl
42. Alkyl halides are prepared from alcohols by treating with
- $HCl + ZnCl_2$
 - Red P + Br_2
 - $H_2SO_4 + KI$
 - All the above
43. Alkyl fluorides are synthesised by heating an alkyl chloride/bromide in presence of _____ or _____
- CaF_2
 - CoF
 - Hg_2F_2
 - NaF

Answers

37. (a), (d) 38. (a), (c) 39. (a), (c) 40. (a), (c) 41. (a), (d) 42. (a), (b) 43. (b), (c)

Multiple Choice Questions

Note : Match the items given in Column I and Column II in the following questions.

44. Match the compounds given in Column I with their effects given in Column II

Column I	Column II
(a) Chloroanaphenol	(i) Malaria
(b) Thyroxene	(ii) Anaesthetic
(c) Chloroquine	(iii) Typhoid fever
(d) Chlorofuran	(iv) Gout
	(v) Blood substituent

45. Match the items of Column I and Column II


Column I	Column II
(a) S_N1 reaction	(i) vic-dibromides
(b) Chemicals in fire extinguisher	(ii) gem-dihalides
(c) Bromination of alkenes	(iii) Racemisation
(d) Alkylidene halides	(iv) Saytzeff rule
(e) Elimination of HX from alkylhalide	(v) Chlorobromocarbon

44. (a) (ii) (b) (v) (c) (i) (d) (iv) (e) (iii)



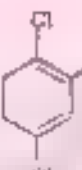




45. (a) (iii) (b) (i) (c) (v) (d) (ii) (e) (iv)

Competition File

46. Match the structures of compounds given in Column I with the classes of compounds given in Column II

Column I	Column II
a) $\text{CH}_3 - \text{CH}(\text{Cl})_2$ X	Aryl halide
b) $\text{CH}_3 - \text{CH}(\text{X}) - \text{CH}_3$ X	(ii) Alkyl halide
c) 	(iii) Vinyl halide
(d) $\text{CH}_2 = \text{CH}-\text{X}$	(iv) Allyl halide

47. Match the reactions given in Column I with the types of reactions given in Column II

Column I	Column II
a)  $\xrightarrow{\text{Fe}/\text{Cl}_2}$  + 	Nucleophilic aromatic substitution
b) $\text{CH}_3 - \text{CH} = \text{CH}_2 + \text{HBr} \rightarrow \text{CH}_3 - \text{CH}_2 - \text{CH}_2\text{Br}$	Electrophilic aromatic substitution
(c)  $\xrightarrow{\text{OH}^-}$ 	Seytzeff elimination
d)  + $\text{NaOH} \rightarrow$ 	(iv) Electrophilic addition
e) $\text{CH}_3\text{CH}_2\text{CH}(\text{Br})\text{CH}_3 \xrightarrow{\text{alc. KOH}} \text{CH}_3\text{CH} = \text{CHCH}_3$	Nucleophilic substitution $\text{S}_{\text{N}}1$

Competition File

48. Match the structures given in Column I with the names in Column II.

Column I	Column II
<p>a. </p> <p>b. </p> <p>c. </p> <p>(d) </p>	<p>i. 4-Bromopent-2-ene</p> <p>ii. 4-Bromo-3-methylpent-2-ene</p> <p>iii) 1-Bromo-2-methylbut-2-ene</p> <p>iv) 1-Bromo-2-methylpent-2-ene</p>

49. Match the reactions given in Column I with the names given in Column II.

Column I	Column II
<p>a. </p> <p>b. </p> <p>(c) </p> <p>(d) </p>	<p>i. Fittig reaction</p> <p>ii. Wurtz Fittig reaction</p> <p>iii) Finkelstein reaction</p> <p>iv) Sandmeyer reaction</p>

48. (a) (i) (b) (ii) (c) (iii) (d) (iv)

49. (a) (i) (b) (ii) (c) (iii) (d) (iv)

Assertion and Reason Type Questions

Note : In the following questions a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices.

- a. Assertion and reason both are correct and reason is correct explanation of assertion
 b. Assertion and reason both are wrong statements
 (c) Assertion is correct but reason is wrong statement
 (d) Assertion is wrong but reason is correct statement.

a. Assertion and reason both are correct statements but reason is not correct explanation of assertion.

50. **Assertion** Phosphorus chlorides (tri and penta) are preferred over thionyl chloride for the preparation of alkyl chlorides from alcohols.

Reason Phosphorus chlorides give pure alkyl halides

51. **Assertion** The boiling points of alkyl halides decrease in the order

$RI > RBr > RCl > RF$

Reason : The boiling points of alkyl chlorides, bromides and iodides are considerably higher than that of the hydrocarbon of comparable molecular mass

50. a

51. a

Competition File

52. **Assertion :** KCN reacts with methyl chloride to give methyl isocyanide
Reason : CN^- is an ambident nucleophile
53. **Assertion :** *tert*-Butyl bromide undergoes Wurtz reaction to give 2, 2, 3, 3-tetramethylbutane
Reason : In Wurtz reaction alkyl halides react with sodium in dry ether to give hydrocarbon containing double the number of carbon atoms present in the halide
54. **Assertion :** Presence of a nitro group at ortho or para position increases the reactivity of haloarene towards nucleophilic substitution.
Reason : Nitro group, being an electron withdrawing group decreases the electron density over the benzene ring.
55. **Assertion :** In monohaloarenes, further electrophilic substitution occurs at ortho and para positions
Reason : Halogen atom is a ring deactivator
56. **Assertion :** Aryl iodides can be prepared by reaction of arenes with iodine in the presence of an oxidising agent
Reason : Oxidising agent oxidises I_2 into HI
57. **Assertion :** It is difficult to replace chlorine by $-\text{OH}$ in chlorobenzene in comparison to that in chloroethane
Reason : Chlorine-carbon $\text{C}-\text{Cl}$ bond in chlorobenzene has a partial double bond character due to resonance.
58. **Assertion :** Hydrolysis of (S)-2-bromooctane proceeds with inversion of configuration.
Reason : This reaction proceeds through the formation of a carbocation.
59. **Assertion :** Nitration of chlorobenzene leads to the formation of *o*-nitrochlorobenzene
Reason : $-\text{NO}_2$ group is a *m*-directing group

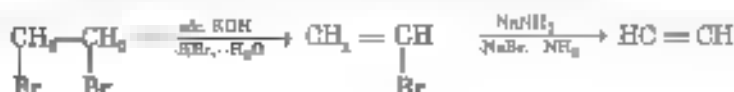
Answers

52. (d) 53. (a) 54. (a) 55. (c) 56. (c) 57. (a) 58. (c) 59. (d)

Hints & Explanations for Difficult Objective Type Questions

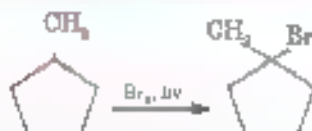
A. mcq with only one correct answer

- A1. **b :** $\text{CH}_3 - \overset{\overset{^1\text{CH}_3}{|}}{\underset{\underset{^3\text{CH}_3}{|}}{\overset{^2\text{C}}{\text{---}}}} - \text{Cl}$ 2-Chloro-2-methylpropane
- A2. **a :** $\overset{^4}{\text{CH}_3} - \overset{^5}{\text{CH}} = \overset{^3}{\text{CH}} - \overset{^1}{\text{CH}_2}\text{Br}$ 1-Bromobut-2-ene.
- A3. **(a) :** $\text{CH}_3\text{CHClCH}_3 \xrightarrow{\text{aq. KOH}} \text{CH}_3\text{CH} \begin{matrix} \text{OH} \\ \text{OH} \end{matrix} \xrightarrow{\text{H}_2\text{O}} \text{CH}_3\text{CHO}$
- A6. **c :** $\text{CH}_3\text{CH}_2\overset{^*}{\text{CH}}\text{ClCH}_2\text{CH}_2\text{CH}_3$ (a) Chiral
 $\text{HOCH}_2\overset{^*}{\text{CH}}\text{COOH}$ (b) Chiral
 $\text{CH}_3\text{CH}(\text{Br})\text{CH}(\text{Br})\text{CH}_3$ (c) Not chiral
 $\text{CH}_3 - \overset{^*}{\text{CH}}(\text{OH})\text{CH}_2\text{CH}_3$ (d) Chiral
- A7. **b :** $\text{CH}_3\text{CH}_2\text{I} \xrightarrow{\text{alc. KOH}} \text{CH}_2 = \text{CH}_2 \xrightarrow{\text{Br}_2/\text{XO}} \begin{matrix} \text{CH}_2 & \text{---} & \text{CH}_2 \\ | & & | \\ \text{Br} & & \text{Br} \end{matrix} \xrightarrow{\text{KCN}} \begin{matrix} (\text{CN})_2 & \text{---} & (\text{CN})_2 \end{matrix}$
- A8. **a :** $\text{CH}_3 - \underset{\underset{\text{Br}}{|}}{\text{CH}} - \text{CH}_2\text{Br} \xrightarrow{\text{alc. KOH}} \text{CH}_2 = \text{CH} - \text{H} \xrightarrow{\text{HBr/Peroxide}} \text{CH}_3 - \text{CH}_2 - \text{CH}_2\text{Br} \xrightarrow{\text{IBr/Peroxide}} \text{CH}_3\text{CH}_2\text{CH}_2\text{IBr}$
- A9. **d :** Simple alkyl halides are dehydrohalogenated by using a strong base such as $\text{alc. K}^+\text{OH}^-$. But vinyl halides require much stronger base such as NaNH_2 for dehydrohalogenation



Competition File

A10. (c) : Ease of abstraction of H is $3^\circ > 2^\circ > 1^\circ$. Therefore, option (c) is correct.

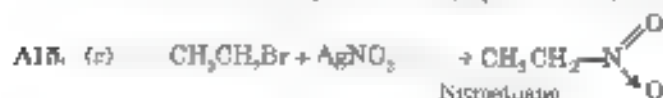


A11. (c) : In the absence of peroxides, the first step is the electrophilic addition i.e. H^+ to form carbocation.

A12. (b) : CH_3O^- is a strong nucleophile as well as a strong base. Therefore, it can either bring about substitution or elimination. Since the CH_3 group at β -carbon causes steric hindrance to nucleophilic substitution ($\text{S}_{\text{N}}2$), therefore, elimination occurs preferably to form 2-methylpropene as.



A13. (b) : With a weak nucleophile such as $\text{C}_2\text{H}_5\text{OH}$, substitution takes place to form *tert*-butyl ethyl ether $\text{H}_3\text{C}-\text{C}(\text{CH}_3)_2-\text{OC}_2\text{H}_5$. A. With a strong base like $\text{C}_2\text{H}_5\text{O}^-$, *tert*-butyl bromide undergoes elimination to form $\text{H}_3\text{C}-\text{C}(\text{CH}_3)=\text{CH}_2$. B.



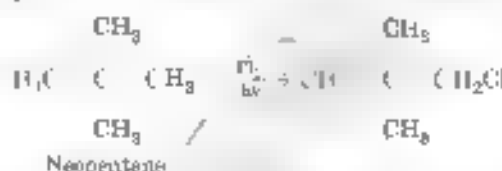
A16. (c) : due to high bond dissociation energy.

A17. (c) : forms three products pentane, butane and hexane.



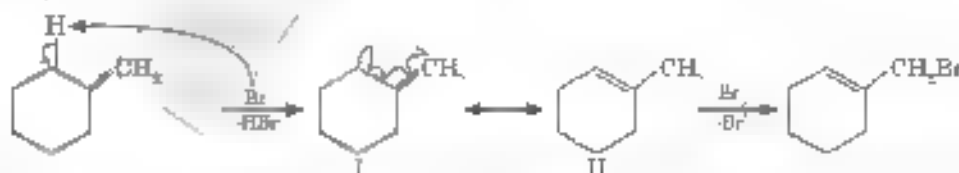
A21. (d) : The halogen atom in vinyl chloride is least reactive.

A22. (d) : Neo-pentane has all the H atoms equivalent and therefore gives only one monochloro derivative.



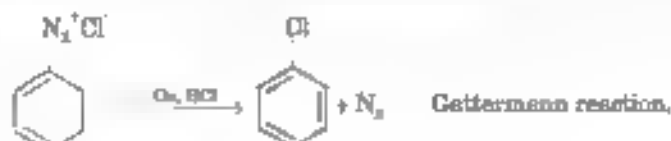
A24. (a) : Smaller the size of the nucleophile (i.e. CH_3O^-) more reactive it is.

A25. (b) : Allylic bromination occurs as



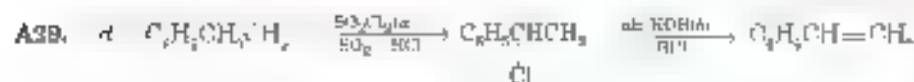
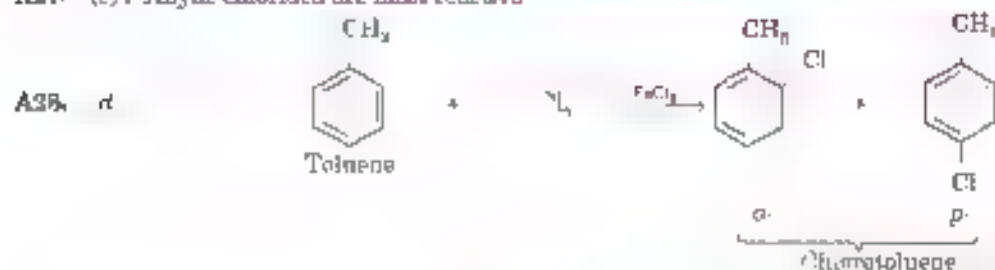
The double bond within the ring (endocyclic radical II) is more stable than the double bond outside the ring (exocyclic radical I). Therefore, the less stable free radical I gets converted into the more stable free radical II which then reacts with Br_2 to give the product.

A26. (a) : Chlorobenzene can be obtained from benzene diazonium chloride by Sandmeyer's or Gattermann reaction.



Competition File

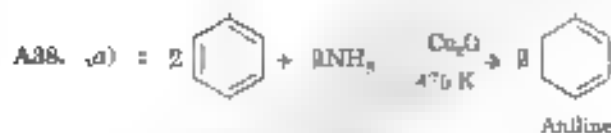
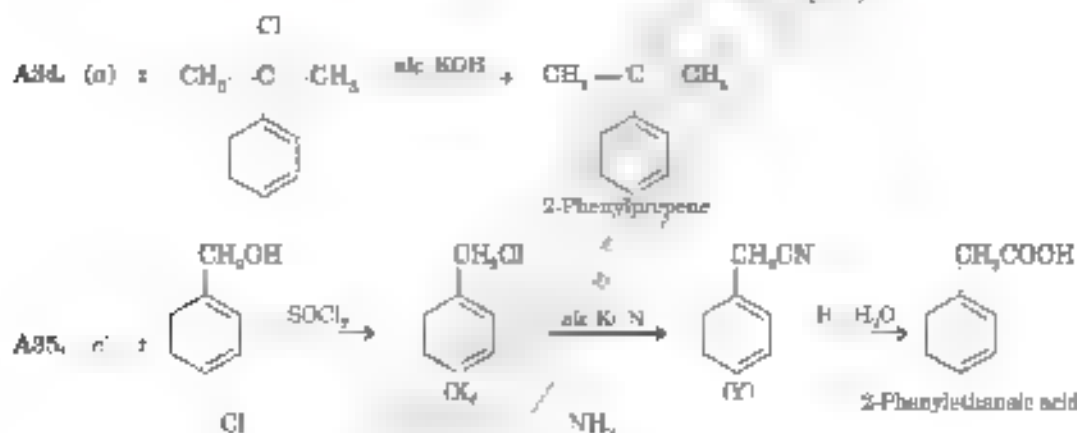
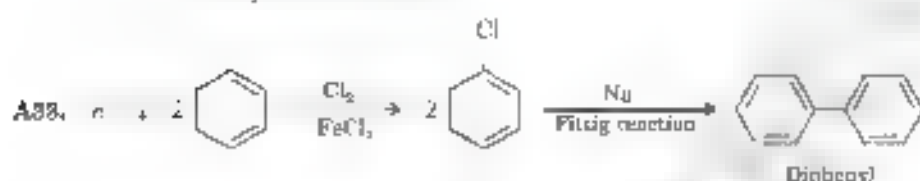
A27. (c) : Aryl chlorides are most reactive



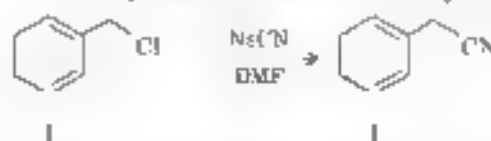
A30. (d) : This is in accordance with the stability of the carbocation as:



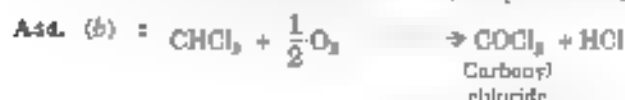
Thus option (d) is correct



A39. (c) : Alkyl halides are more reactive than aryl halides and therefore only the side chain halogen, Cl is displaced



A40. (c) : Alkyl halides are more reactive than aryl halides. (a) and (d) are aryl halides and therefore less reactive than alkyl halides (b) and (c). Since precipitate has yellow colour it must be AgI. So, option (c) is correct



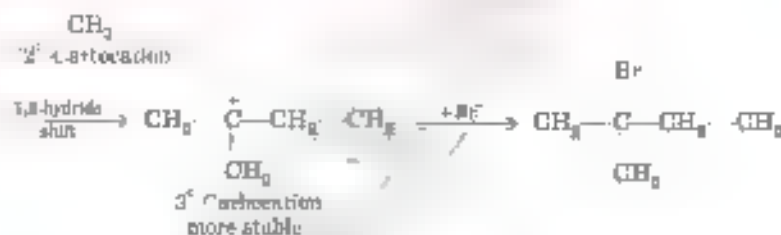
Competition File

B. mcq from competitive examinations

B1. (a) The nucleophilicity increases as $\text{Cl}^- < \text{Br}^- < \text{I}^-$

B2. (c) : Rate of $\text{S}_{\text{N}}2$ reaction decreases with increase in steric hindrance. Since CH_3I has the least steric hindrance, it reacts at the fastest rate.

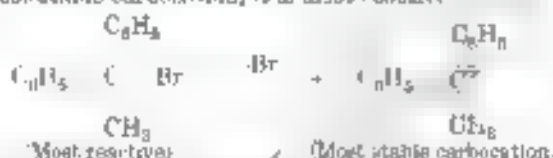
B3. (a) : $\text{CH}_3\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}_2 + \text{HBr} \xrightarrow{\text{Br}^-} \text{CH}_3\text{CH}_2\text{CH}^+\text{CH}_2\text{CH}_3$



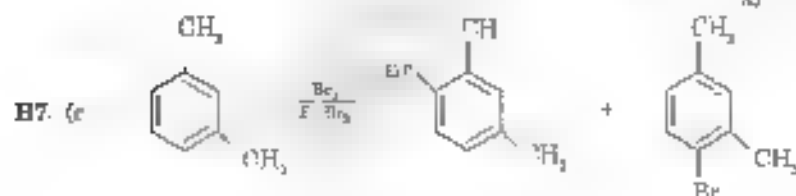
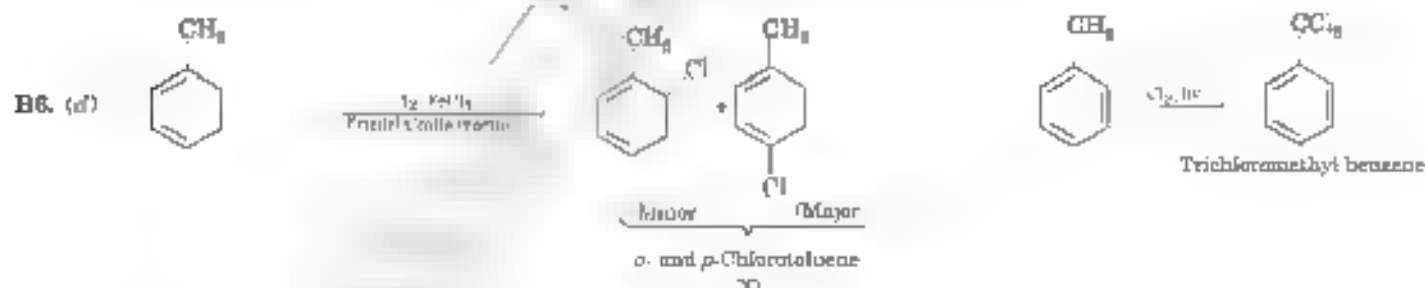
B4. (a) For $\text{S}_{\text{N}}1$ reactions, more stable is the carbocation, more reactive is alkyl halide. The stability of carbocations increases in the order



Since (a) forms the most stable carbocation, it is most reactive.



B5. (a) : The order of reactivity depends upon the stability of carbocation formed by the cleavage of $\text{C}-\text{X}$ bond. The 3° carbocation formed from III will be more stable than 2° carbocation formed from IV. The 2° carbocation formed from IV will be more stable than the primary ion formed from I because aryl halides are less reactive than alkyl halides. However I will be more reactive than II due to the presence of the electron withdrawing NO_2 group which makes $\text{C}-\text{X}$ bond weak and undergoes nucleophilic substitution reaction faster. Thus correct order is

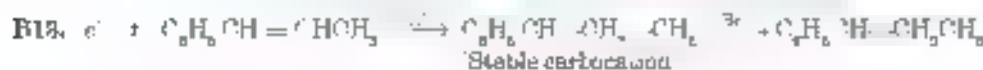
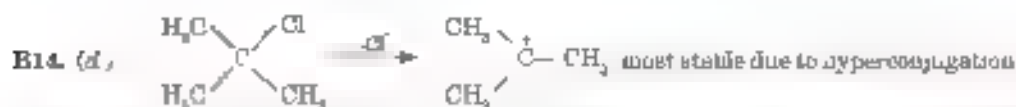


B8. (d) Due to chirality of $\left(\text{H}-\text{C}-\text{Cl}\right)$ only compound (d) will undergo racemisation.



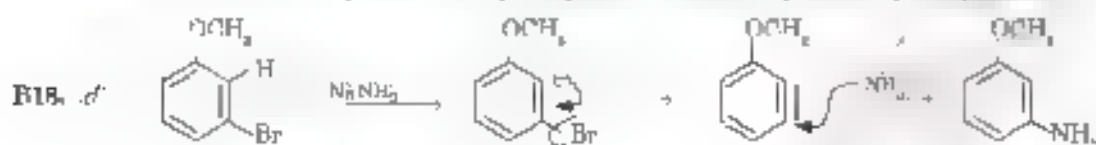
Competition File

B11 $c + 1^{\circ}$ and 2° alcohol react with H^+ in the presence of anhydrous Zn^{+2} while in case of 3° alcohol anhydrous Zn^{+2} is not needed. Therefore alkyl halides can be prepared by reactions I, II and IV.

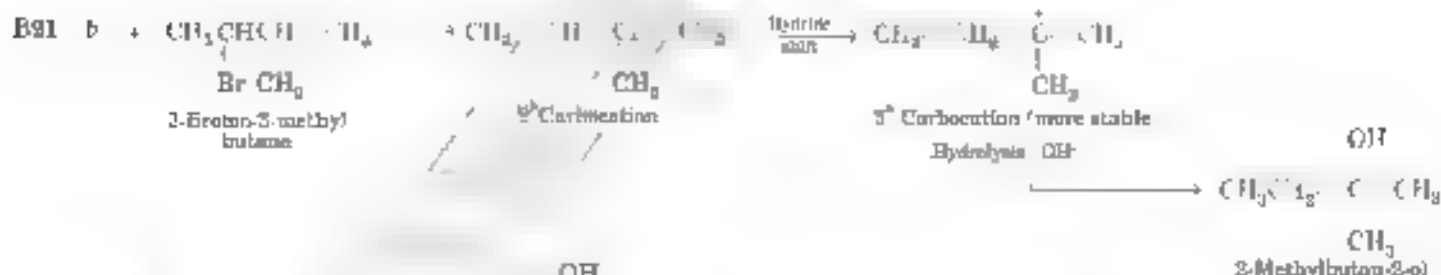
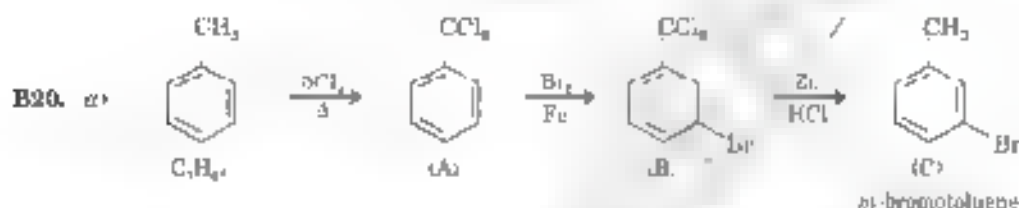
 \dot{B}_T 

B16. $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{Br}$ is a primary halide. Therefore it undergoes nucleophilic substitution via $\text{S}_{\text{N}}2$ mechanism. $\text{S}_{\text{N}}2$ reaction is fastest in aprotic solvents (DMF).

B17. d This is a biphenyl system in which ortho positions are occupied by groups and both the rings are not in one plane. Therefore their mirror images are non-superimposable and the compound is optically active.



It is subject to union regulation.



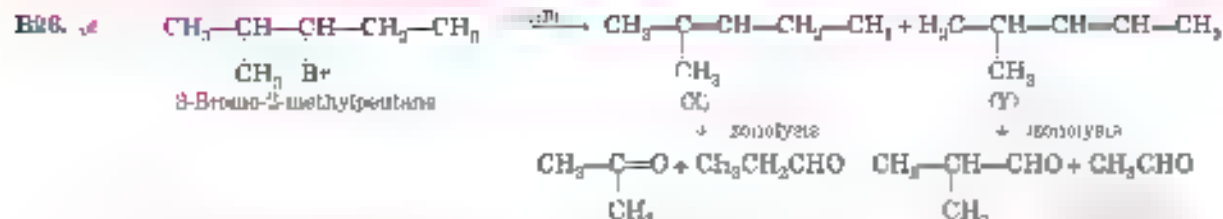
Ex4. a) : The decreasing order of reactivity towards S_N2 reactions is



This is because of increasing static hindrance.

B25. c. Tertiary alkyl halides undergo S_N1 reaction and the rate depends only on the concentration of alkyl halide

Competition File



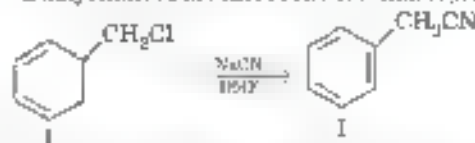
B27. (b) Aryl halides ($\text{C}_6\text{H}_5\text{Cl}$) do not undergo hydrolysis by $\text{S}_{\text{N}}1$ mechanism under ordinary conditions.



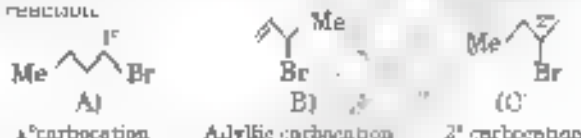
B30. (c) Neopentyl chloride does not have any β -hydrogen and hence it does not undergo dehydrohalogenation reaction.

B31. (c) The reaction follows $\text{S}_{\text{N}}2$ mechanism so stronger the base the better its nucleophilicity as $\text{CH}_3\text{O}^- > \text{OH}^- > \text{PhO}^- > \text{AcO}^-$.

B32. (c) Aryl halides are more reactive than alkyl halides and, therefore, only the halogen in the side chain is the substituted.



B33. (c) Formation of carbocation is the rate determining step in $\text{S}_{\text{N}}1$ reaction. Therefore, the reactivity in $\text{S}_{\text{N}}1$ reactions depends upon the stability of the intermediate carbocation. The alkyl halide which gives more stable carbocation is more reactive towards $\text{S}_{\text{N}}1$ reaction.



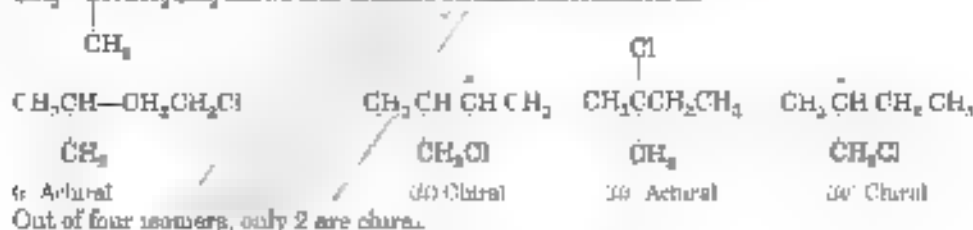
It involves 1° carbocation Allylic carbocation 2° carbocation

Order of stability of carbocation is

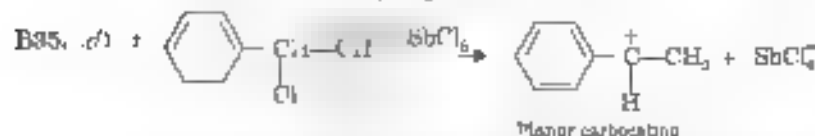
Allyl $>$ $3^\circ >$ $2^\circ >$ 1°

Order of reactivity is $\text{B} >$ $\text{C} >$ A . Therefore, option (c) is correct.

B34. (a) $\text{CH}_3-\text{CH}(\text{CH}_3)-\text{CH}_2-\text{CH}_3$ shows four isomers on monochlorination as

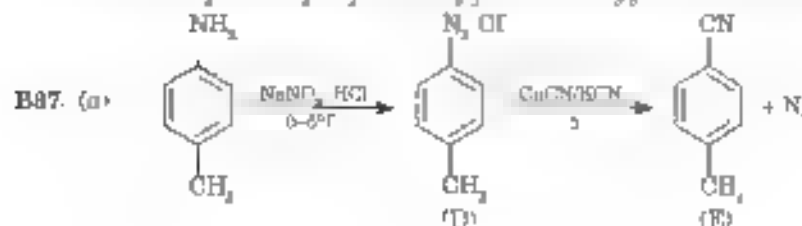


Out of four isomers, only 2 are chiral.

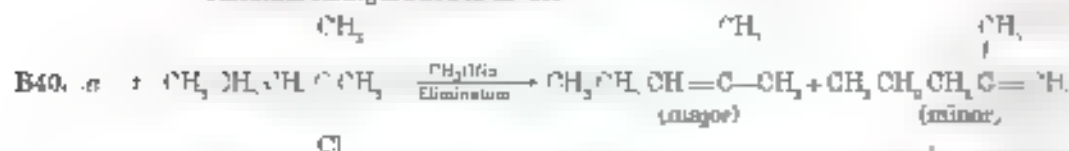
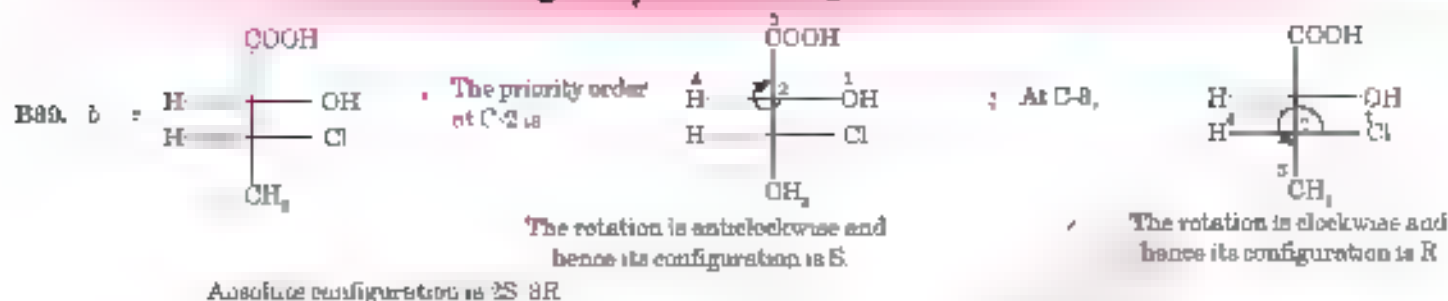


The carbocation is subsequently attacked both from top and bottom to give racemic mixture.

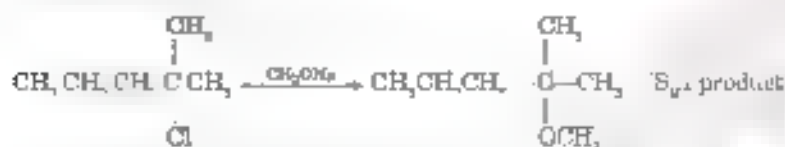
B36. (c) Rate of reaction depends on steric crowding of alkyl halide. Therefore, the order of reactivity is $\text{CH}_3\text{Cl} >$ $\text{CH}_3\text{CH}_2\text{Cl} >$ $(\text{CH}_3)_2\text{CHCl} >$ $(\text{CH}_3)_3\text{CCl}$.



Competition File

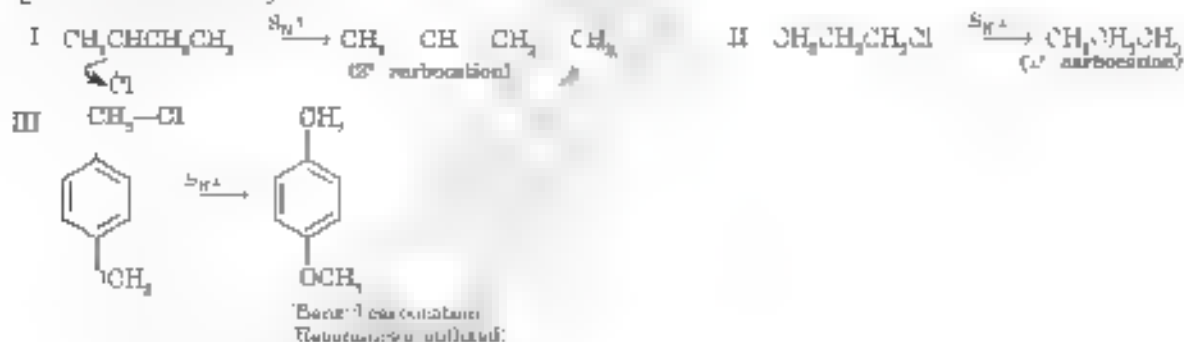


In this reaction, elimination occurs because 2-chloro-2-methylpentane is a 3° alkyl halide. It can not undergo nucleophilic substitution reaction as:



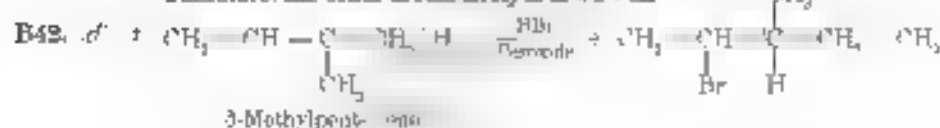
Therefore all of these will be formed

B41. b : In S_N1 reaction, the stability of carbocation formed determines the reactivity. Greater the stability of the carbocation, greater is the reactivity.

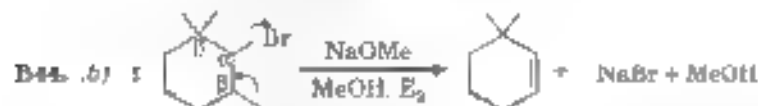
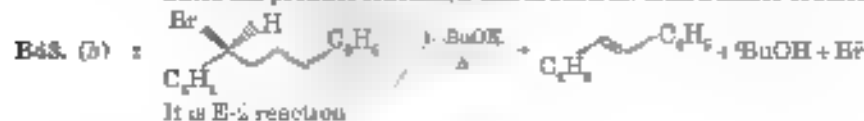


The order of stability of carbocation is: II < I < III

Therefore, the order of reactivity is II < I < III



Since the product contains 2-chiral centres, total number of stereoisomers = $2^2 = 4$



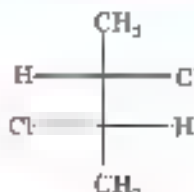
B45. c : Aryl halides are more reactive than alkyl halides and, therefore, only b and c will react. Since precipitate has yellow colour, it must be of AgI. Hence, option (c) is correct.

B46. a : The addition of HBr to symmetrical alkenes (2-butene) is not affected by the presence or absence of peroxide.



Competition File

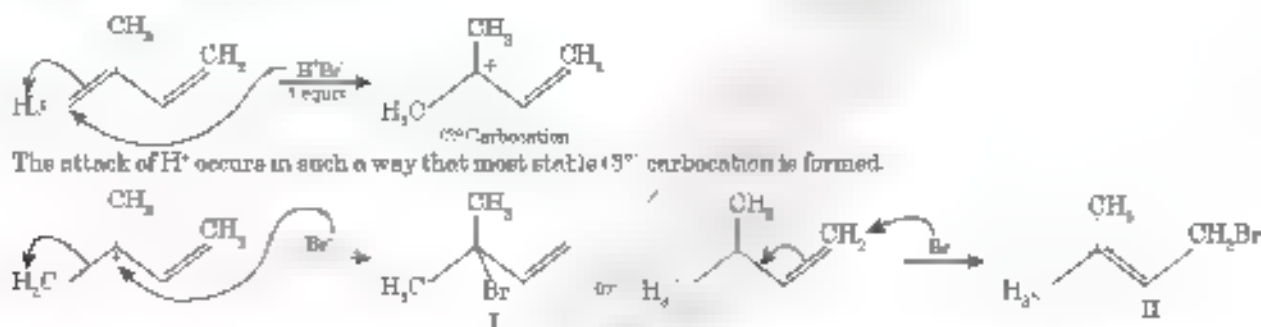
B70. (a) : The compound has two chiral centres and hence is optically active



B71. (b) The bulky groups result into steric hindrance in the formation of transition state. Therefore, **H** is less reactive than **P**. In the compound **S**, the transition state is highly stabilized by $\text{Ph}-\text{C}=\text{O}$ group and hence it is most reactive. Hence the

order of reactivity is $\text{S} > \text{P} > \text{R} > \text{Q}$

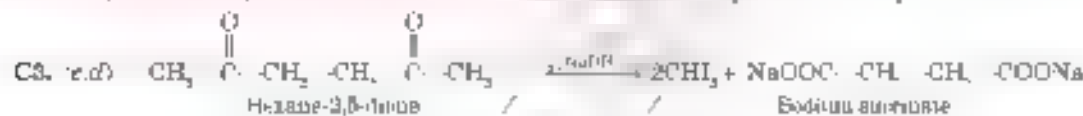
B72. (a) :



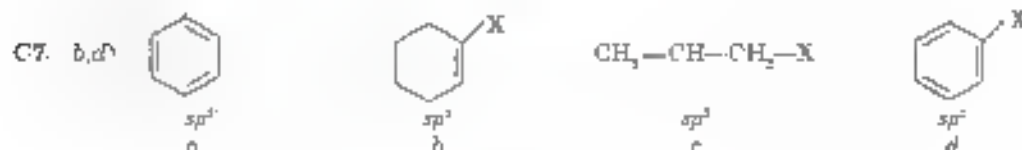
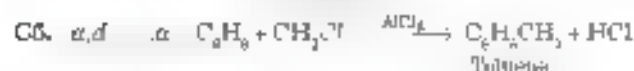
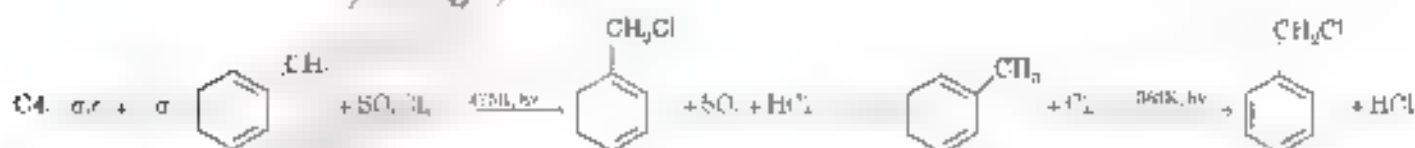
Product **I** is the major product, in accordance with Markovnikoff rule, more substituted alkene is more stable.

C. mcq with more than one answers

C1. a, b, d Except for *trans*-1,2-dichloroethene, *cis* isomers have dipole moment.

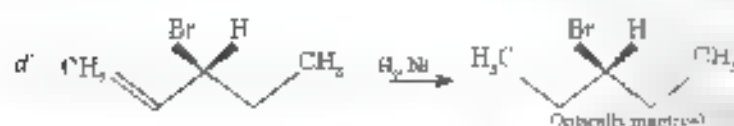
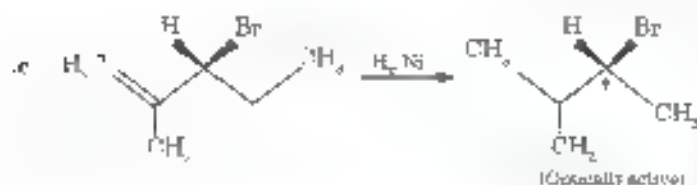
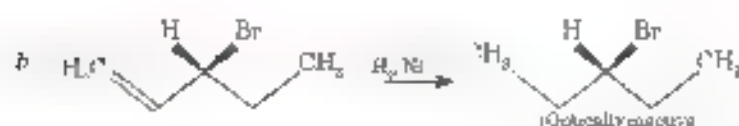
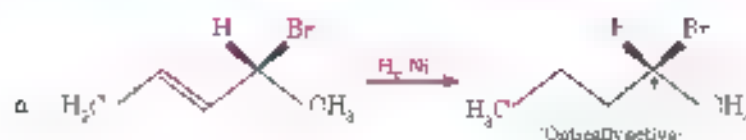


Compounds having $\text{CH}_3\text{C}(=\text{O})$ group give iodoform test.



Competition File

C8. (b,d)

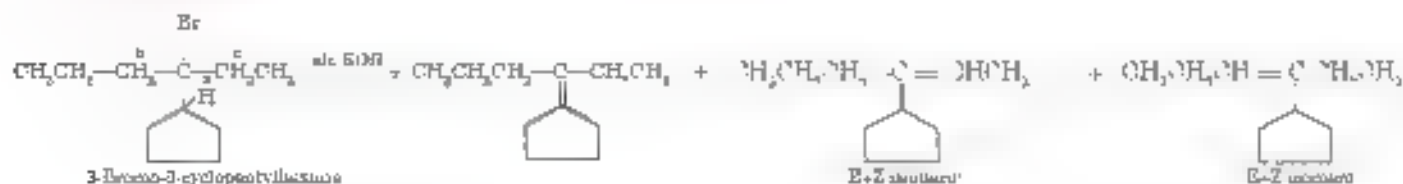
C10. (a,b,d) : (a) I and II follow S_N2 mechanism. 1° halides.

c The order is not correct.

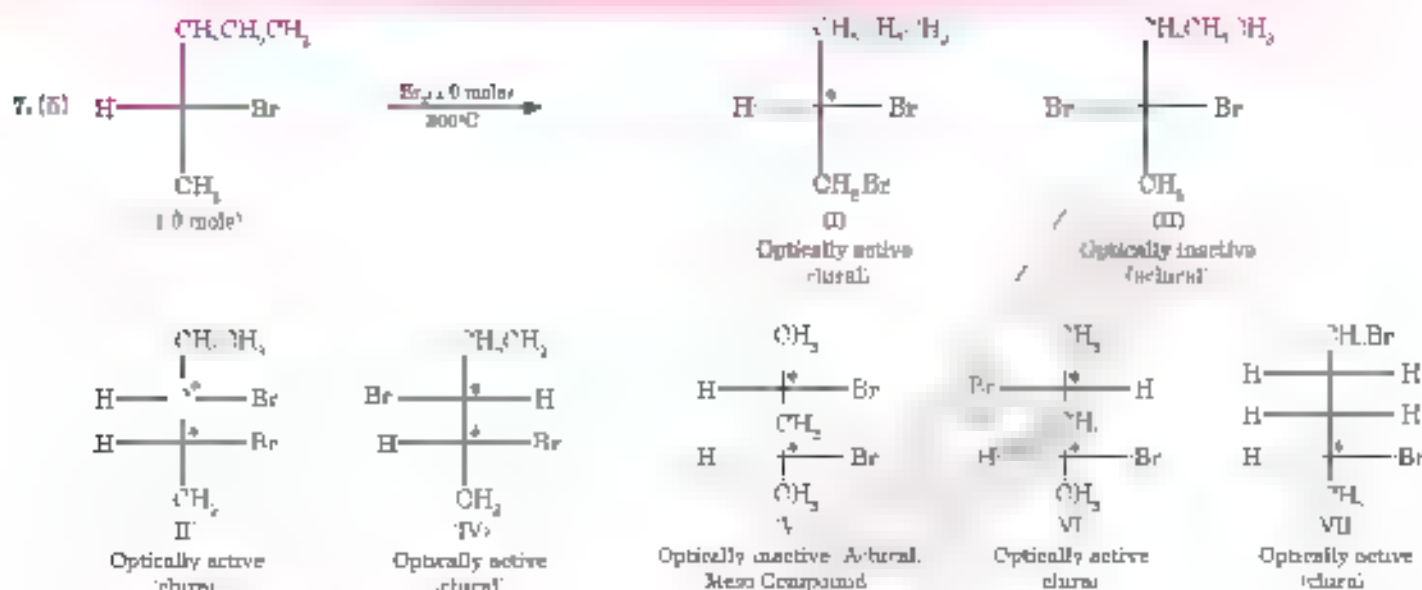
d I is benzyl halide, and III is 3° alkyl halide and follow S_N1 mechanism.

Integer Type Questions

- 4 The compounds having chiral carbon and therefore, showing enantiomers are: Butan-2-ol, 2-Hydroxypropanoic acid, 2-chlorobutane, 2-Bromo-2-chlorobutane.
- 3 (ii), (iv), (v)
- 5 (ii), (iii), (v), (vi), (vii)
- 1 (v)
- 8) See Solvent Example 4, page 12
- 5 *d*-Bromo-3-cyclopentylhexane has three different types of α -hydrogen atoms marked a, b and c and hence give three structurally isomeric alkenes. Two of these can exhibit geometrical isomerism and therefore, the total number of alkenes possible are five.



Competition File



Total five optically active products I, III, IV, VI and VII are formed.

NCERT Exemplar Problems MCQs Type-I

- (b). Reactivity of alcohols towards halogen acids is $3^\circ > 2^\circ > 1^\circ$
- (d) 3° is most reactive
- (a)
- (a) Density increases as molecular mass increases i.e. I < II < III < IV
- (c) Boiling points increase as branching decreases i.e. III < I < II
- (b) Carbon attached to four different atoms or groups is asymmetric
- (a) It is allylic compound in which Br is attached next to double bonded carbon.
- (c) Markovnikov's rule is followed
- (b) Primary alkyl halide would prefer to undergo S_N2 reaction
- (a). Because carbocation will be readily formed.
- (c)
- (b)
- (d) Cl group is o, p-directing group
- (a) $\text{CH}_3\text{Cl} + \text{NH}_3$ (excess) $\rightarrow \text{CH}_3\text{NH}_2 + \text{HCl}$
- (a)
- (a). $\text{C}_6\text{H}_5\text{CH}_3$ is stable carbocation and therefore, favours S_N1 reaction
- (b). (i) and (ii) carbon atoms are asymmetric
- (a). only (i) because it proceeds through formation of carbocation.

NCERT Exemplar Problems MCQs Type-II

- (a), (c)
- (a), (c)
- (a), (d)
- (b), (c) $\text{BCl}_3 + \text{Hg}_2\text{F}_2/\text{CoF}_2 \rightarrow \text{RF}$

Unit Practice Test

for Board Examination

Time Allowed : 2 Hrs.

Maximum Marks : 35

- Which isomer of C_4H_9Cl will have the lowest boiling point? (1)
- Write the formula of the main product formed in the reaction

$$CH_3CH=CH_2 \xrightarrow[\text{Dry ether}]{Na} \quad \quad \quad$$
 (1)
- How will you convert propene into allyl iodide? Give equation. (1)
- Why does iodoform has appreciable antiseptic property? (1)
- How will you convert propene to propyne? (1)
- Out of $C_6H_5CH_2Cl$ and $C_6H_5CH(Cl)CH_3$, which is more easily hydrolysed by aqueous KOH ? Why? (2)
- Which compound in each of the following pairs will react faster in S_N2 reaction with OH^- ? (2)
 - CH_3Br or CH_3I
 - $(CH_3)_3CCl$ or CH_3Cl
- Write the IUPAC names of the following. (2)

(b) $CH_3CH=CH-C(CH_3)_2Br$
- Describe the role of Lewis acids in the preparation of aryl bromides and chlorides in the dark. (2)
- Why is the solubility of haloalkanes in water very low? (2)
- How will you distinguish between: (3)
 - Ethyl chloride and ethyl bromide
 - Chlorobenzene and cyclohexyl chloride
 - Vinyl chloride and ethyl chloride
- How do the products differ when ethyl bromide react with HCN and $AgCN$? Give reasons. (3)
- How would you distinguish between S_N1 and S_N2 mechanisms of substitution reactions? Give one example of each. (3)
- How will you convert: (3)
 - Ethyl chloride to propanoic acid
 - 1-Bromopropane to 3-bromopropane
 - tert-butyl bromide to isobutyl bromide
- (a) Grignard reagent should be prepared under anhydrous conditions? Explain. (3)
 - Give two uses of iodoform.
 - Write the structure and formula of DDT.
- (a) Why are haloarenes less reactive than haloalkanes? Explain. (3)
 - Predict the alkenes that would be formed by dehydrohalogenation of the following halides with sodium ethoxide in ethanol and predict the major alkene.
 - 2-chloro-2-methylbutane
 - 3-bromo-2,2,3-trimethylpentane
 - How is chlorobenzene prepared from benzenediazonium chloride? (3)

► To check your performance see HINTS AND SOLUTIONS TO SOME QUESTIONS at the end of Part II of the book

11 ALCOHOLS, PHENOLS AND ETHERS

विद्यया ऽ मृतमश्नुते

Building on...

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CHAPTER SUMMARY & QUICK CHAPTER ROUND UP

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NCERT FILE

- In-text Qs & Exercises with Solutions 81
- NCERT Exemplar Problems with Answers & Solutions (Subjective) 96

Assessing...

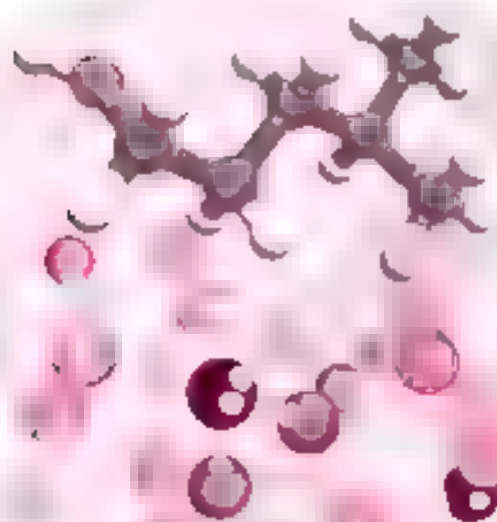
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UNIT PRACTICE TEST

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Preparing for Competition

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Alcohols are the compounds that have one or more hydroxyl (-OH) groups bonded to aliphatic carbon atoms while phenols are the compounds which have one or more -OH groups bonded to the aryl carbon atoms (aromatic rings). These are obtained by replacing one or more hydrogen atoms of aliphatic or aromatic hydrocarbons by hydroxyl (-OH) group.

The compounds obtained by replacing one hydrogen atom from aliphatic hydrocarbons by hydroxyl group are alcohols whereas those obtained by replacing hydrogen atom of aromatic hydrocarbons are phenols.



Alcohols have many important applications in day-to-day life. For example, ethanol (C_2H_5OH), simply called alcohol, is widely used as an important component of alcoholic beverages, as a solvent for many medicines, liquors and varnishes. It is also used in the form of rectified spirit or polishing wooden furniture and as an antiseptic. Phenols are also used for the manufacture of dyes, resins, plastics, etc. In fact, alcohols are very popularly used for the synthesis of other classes of organic compounds such as alkanes, haloalkanes, ethers, aldehydes, ketones, acids, etc.

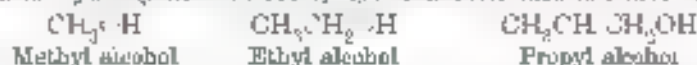
The substitution of a hydrogen atom in a hydrocarbon by an alkoxy (RO) or aryloxy group (ArO) gives another class of compounds known as **ethers**. These are also an important class of compounds. For example, diethyl ether has been extensively used as an industrial solvent.

PART A

ALCOHOLS AND PHENOLS

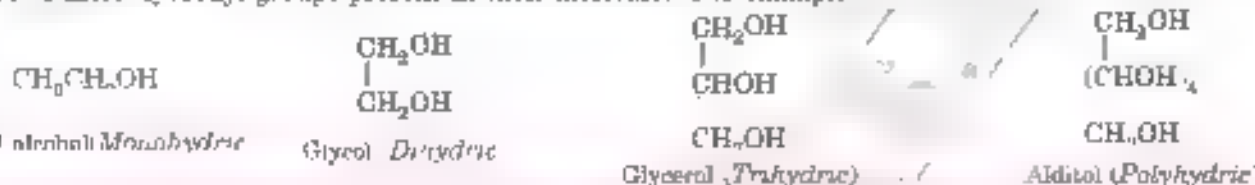
CLASSIFICATION OF ALCOHOLS AND PHENOLS

Alcohols are the compounds containing hydroxyl group $-OH$ attached to the alkyl group. Therefore, these are regarded as hydroxy derivatives of hydrocarbons and are also called **aliphatic alcohols**. For example,

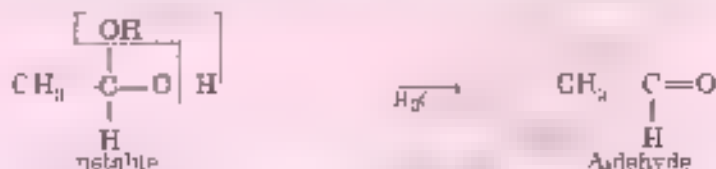


The alcohols are represented by the general formula ROH .

The alcohols are further classified as **monohydric**, **dihydric**, **trihydric** or **polyhydric** alcohols depending upon the two, three or more hydroxyl groups present in their molecules. For example



It may be noted that more than one OH groups cannot be present on the same carbon atom. In such a case, the compound will be extremely unstable and will readily lose a water molecule to form more stable aldehyde, ketone or carboxylic acid.

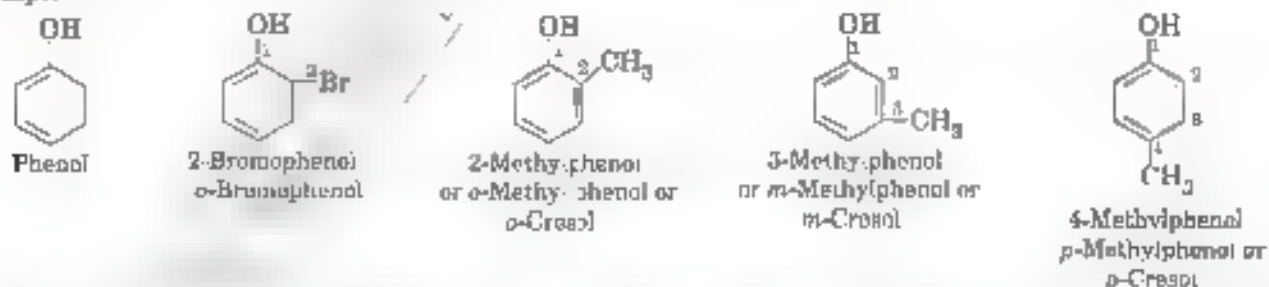


Similarly, if three OH groups are present on the same carbon atom, the molecule loses a molecule of water to form carboxylic acid.

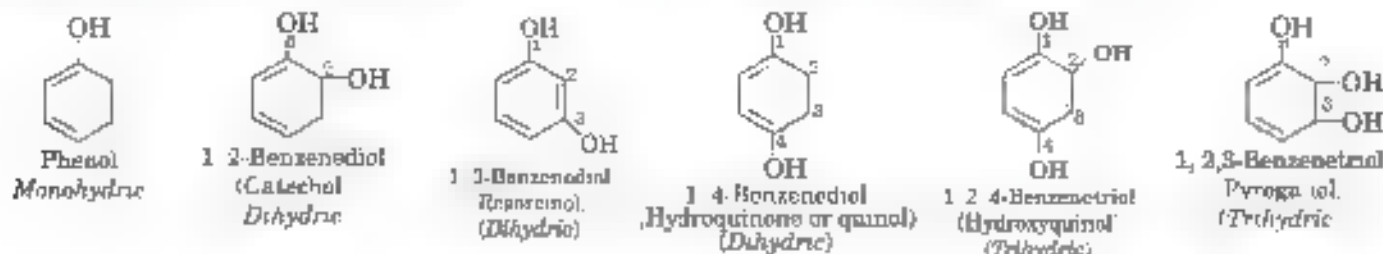


Phenols are hydroxyl derivatives of aromatic hydrocarbons in which the hydroxyl group $-OH$ is directly attached to the carbon atom of the aromatic ring.

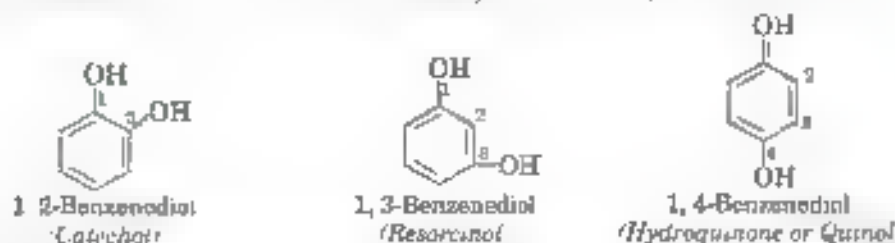
For example,



Like alcohols, phenols may also be classified as **monohydric**, **dihydric**, **trihydric** or **polyhydric** according as their molecules contain one, two, three or more hydroxyl groups respectively. These compounds are popularly known by their common names. For example,



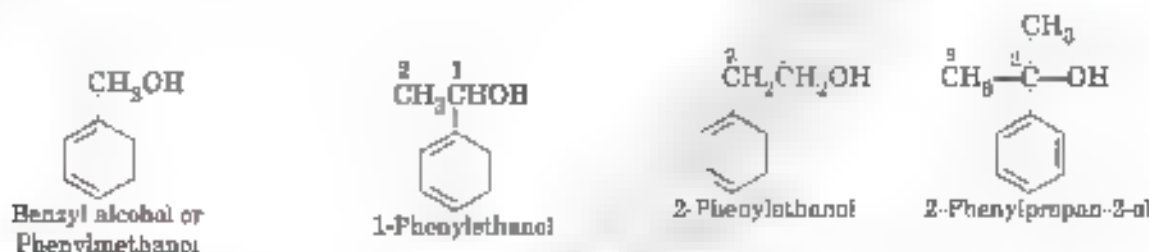
Dihydric derivatives of benzene are known as 1,2-, 1,3- and 1,4-benzenediol



Aromatic alcohols

It may be noted that if the hydroxy group ($-OH$) is not directly linked with benzene ring and is present in the alkyl side chain, then the compound is not a phenol. It is called **aromatic alcohol** because it resembles aliphatic alcohols in its characteristics. Thus, the **aromatic alcohols** are those in which the hydroxyl group is present in the side chain of an aromatic hydrocarbon.

For example,



Classification of alcohols

Monohydric alcohols may be classified on the basis of hybridisation of the carbon atom to which the hydroxyl group ($-OH$) is attached.

1. Compounds containing $C_{sp^3}-OH$ bond

In this type of alcohols, the hydroxyl group ($-OH$) is attached to an sp^3 hybridised carbon atom of an alkyl group. They are further classified as follows:

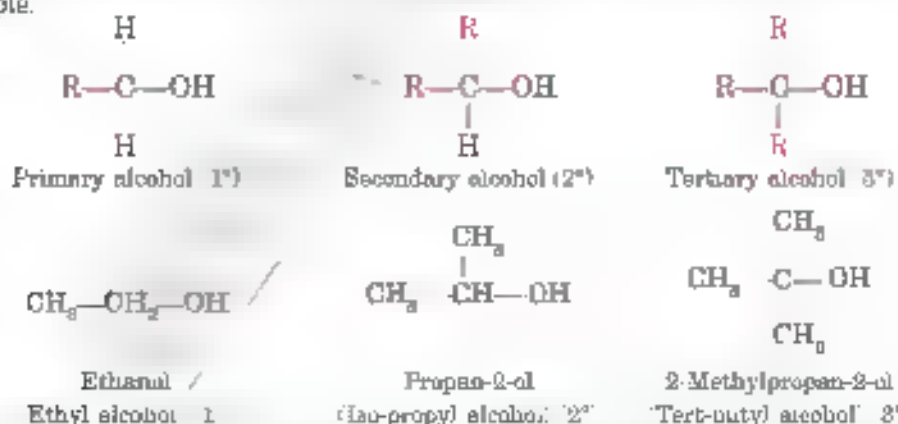
(a) **Primary, secondary and tertiary alcohols:** The alcohols are classified as *primary*, *secondary* and *tertiary* alcohols depending upon the hydroxyl group attached to a primary, secondary or a tertiary carbon atom.

(i) **Primary alcohols (1°)** which have one or more alkyl groups on the carbon bonded to $-OH$ group.

(ii) **Secondary alcohols (2°)** which have two alkyl groups on the carbon bonded to $-OH$ group.

(iii) **Tertiary alcohols (3°)** which have three alkyl groups on the carbon bonded to $-OH$ group.

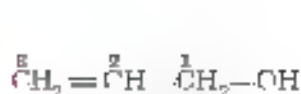
For example,



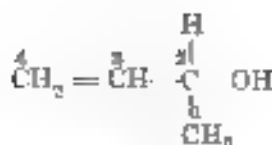
Thus, it is clear from the above structures that the characteristic functional groups of primary, secondary and tertiary alcohols are:



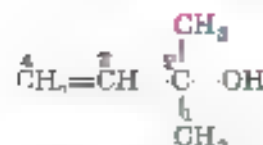
(b) **Allylic alcohols:** In these alcohols, the hydroxyl group is attached to a sp^3 hybridised carbon next to a carbon-carbon double bond known as allylic carbon. These alcohols can also be classified as primary, secondary or tertiary allylic alcohols. For example,



Prop-2-en-1-ol
1° Alkyl alcohol

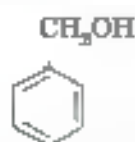


But-3-en-2-ol
2° Alkyl alcohol

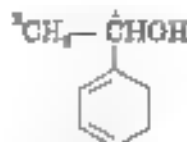


2-Methylbut-3-en-2-ol
3° Alkyl alcohol

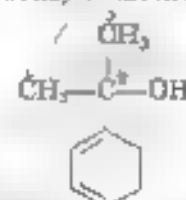
(c) **Benzyl alcohols.** In these alcohols, the hydroxyl group $-\text{OH}$ is attached to a sp^3 hybridised carbon atom next to an aromatic ring. These alcohols may also be classified as 1°, 2° and 3° benzylic alcohols.



Benzyl alcohol (1°)



1-Phenylethanol (2°) / 2-Phenylpropan-2-ol (3°)



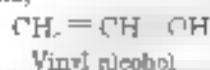
These are also called **aromatic alcohols**.

2. Compounds containing $\text{C}_{\text{sp}^2}-\text{OH}$ bond

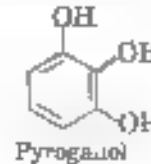
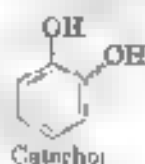
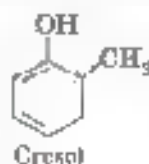
In this type of alcohols, the hydroxyl group $-\text{OH}$ is attached to a carbon-carbon double bond.

These are of two types

(a) **Vinyl alcohols.** These contain $-\text{OH}$ group attached to a carbon atom of a carbon-carbon double bond. These alcohols are called vinyl alcohols. For example,



(b) **Phenols.** These contain $-\text{OH}$ group attached to a carbon atom of benzene ring. For example,

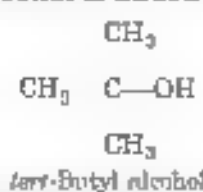
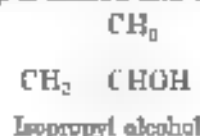
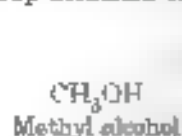


NOMENCLATURE

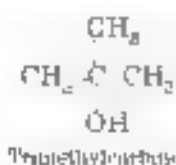
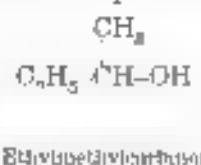
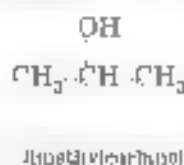
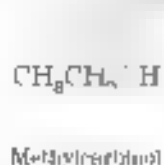
Nomenclature of Alcohols

(a) Monohydric alcohols.

(i) **Common names.** According to common system of nomenclature, alcohols are named as *alkyl alcohols* in which the alkyl group attached to the $-\text{OH}$ group is named and the word **alcohol** is added to it. For example,



(ii) **Carbinol system.** In this system, the simplest monohydric alcohol, CH_3OH is called carbinol while other alcohols are named as alkyl derivatives of carbinol. For example,



(iii) **IUPAC system.** According to IUPAC nomenclature, alcohols are named by replacing 'e' in the name of parent alkane by 'ol'.

Alkane + e + ol = Alkanol

In this system, the following rules are followed

The longest continuous chain containing the carbon bonded to $-\text{OH}$ group is selected as the parent chain.

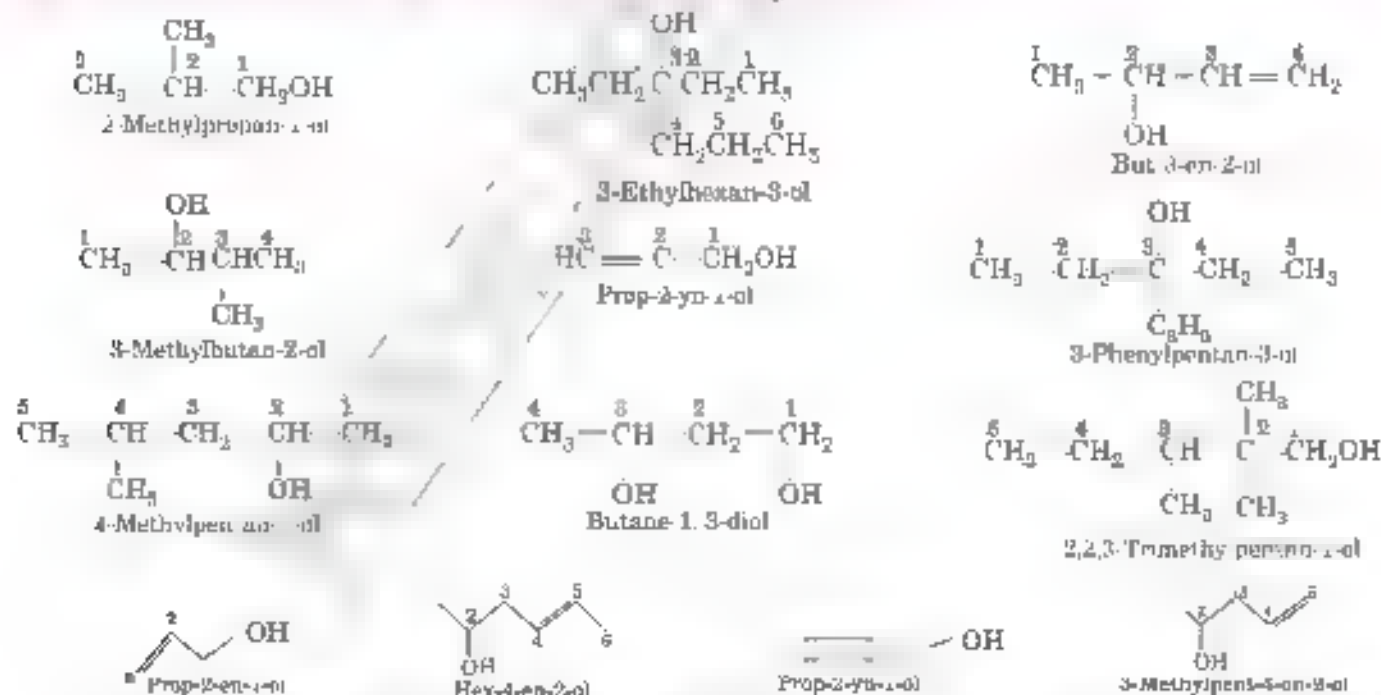
The carbon atoms in the chain are numbered in such a way that the carbon atom carrying the hydroxyl group $-\text{OH}$ gets the lowest number.

The position of the substituents is indicated by suitable numbers.

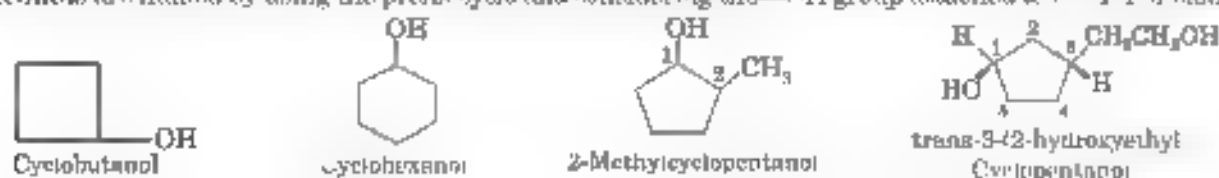
The common and IUPAC names of a few monohydric alcohols are given below

Formula	Common name	IUPAC name
CH_3OH	Methyl alcohol	Methanol
$\text{CH}_3\text{CH}_2\text{OH}$	Ethyl alcohol	Ethanol
$\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$	n-Propyl alcohol	Propan-1-ol
$(\text{CH}_3)_2\text{CHCH}_2\text{OH}$	Isopropyl alcohol	Propan-2-ol
$\begin{array}{c} \text{OH} \\ \\ \text{CH}_3\text{CHOHCH}_2\text{CH}_3 \end{array}$	sec-Butyl alcohol	Butan-2-ol
$\begin{array}{c} \text{OH} \\ \\ \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH} \end{array}$	n-Butyl alcohol	Butan-1-ol
$\begin{array}{c} \text{OH} \\ \\ \text{CH}_3\text{CHCH}_2\text{OH} \end{array}$	Isobutyl alcohol	2-Methylpropan-1-ol
$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_2 \\ \\ \text{CH}_2-\text{C}-\text{OH} \end{array}$	tert-Butyl alcohol	2-Methylpropan-2-ol
$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3-\text{CH}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{OH} \end{array}$	n-Amyl alcohol	Pentan-1-ol
$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3-\text{CH}-\text{CH}_2-\text{CH}_2-\text{OH} \end{array}$	Isoamyl alcohol	3-Methylbutan-1-ol

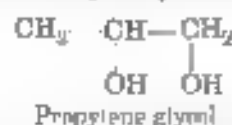
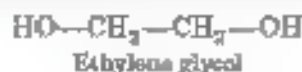
The IUPAC names of a few other substituted alcohols are given below



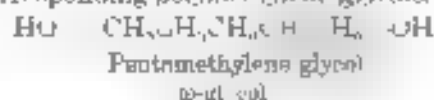
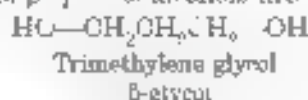
Cyclic alcohols are named by using the prefix cyclo and considering the —OH group attached to C-1. For example,



b) Polyhydric alcohols. These contain two or more OH groups in their molecules. The dihydric alcohols (containing two OH groups) are called **glycols**. These are defined as α , β , γ glycols depending upon the relative positions of the two hydroxyl groups. For example, α -glycol is 1,2-glycol, β -glycol is 1,3 and γ -glycol has two OH groups attached to the terminal carbon atoms. In common system, α -glycols are named by adding the word glycol to the name of the alkene from which they can be obtained by direct hydroxylation. For example



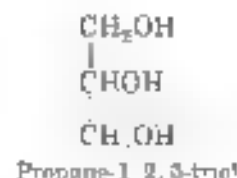
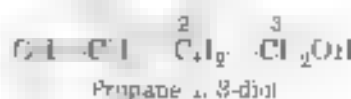
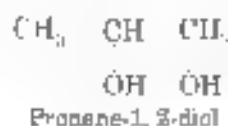
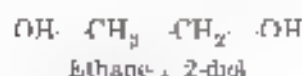
On the other hand, β , γ glycols are named as the corresponding *polymethylene glycols*. For example,



The trihydric alcohols do not have any general rules for naming. The common example is

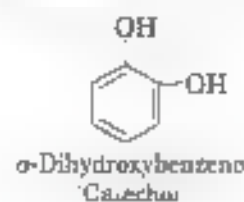
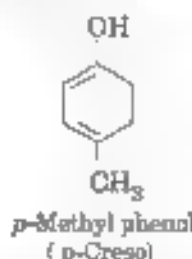
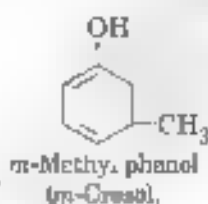
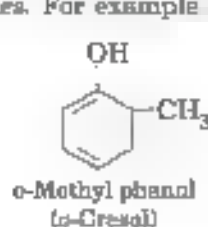


In **IUPAC system** polyhydric alcohols are easily named as *diols, triols* etc., indicating the position of hydroxyl groups. For example,

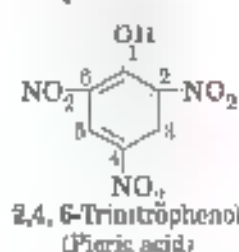
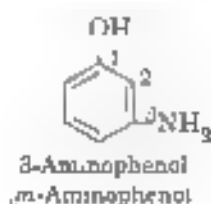
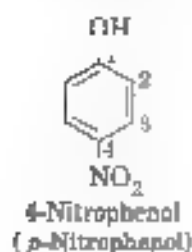
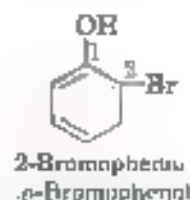
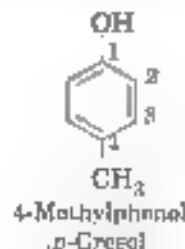
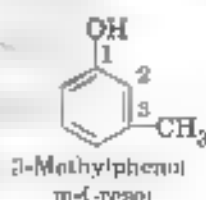
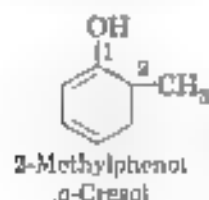


Nomenclature of Phenols

According to **common system** of nomenclature, the parent member of the family is **phenol**. The other members are named as *derivatives of phenol*. The position of the substituents is indicated by the prefixes *ortho* (*o*- for 1,2; *meta* (*m*- for 1,3) and *para* (*p*- for 1,4). However, some substituted phenols are still popularly known by their *trivial names*. For example



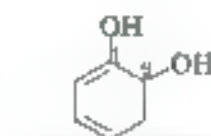
According to **IUPAC system** also, all the substituted phenols are named as derivatives of phenols. The position of the substituents w.r.t. OH group is indicated by Arabic numerals with the carbon carrying OH group being numbered 1). For example,



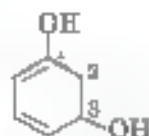
REMEMBER

2,4,6-Trinitrophenol is popularly known as **picric acid**.

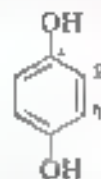
In IUPAC system, di, tri or polyhydric phenols are named as hydroxy derivatives of benzene. However, they are popularly known by their common names. For example,



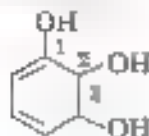
Benzene-1,2-diol
(Catechol)



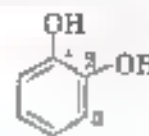
Benzene-1,3-diol
(Resorcinol)



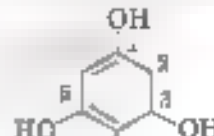
Benzene-1,4-diol
(Hydroquinone or quinone)



Benzene-1,2,3-triol
(Pyrogallol)

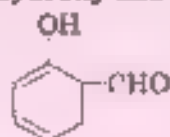


Benzene-1,2,4-triol
(Hydroxyquinol)

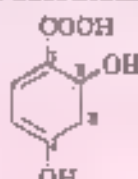


Benzene-1,3,5-triol
(Phloroglucinol)

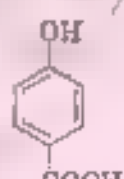
It may be noted that certain groups such as **carbonyl** (aldehydic, ketonic or acidic) or **acyl group** etc. take preference over the phenolic -OH group in determining the parent name. In these cases, the phenolic group is named as **hydroxy** and is treated as a substituent.



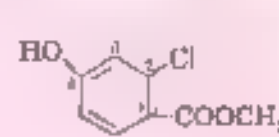
2-Hydroxybenzaldehyde
(o-Hydroxy benzaldehyde
or salicylaldehyde)



4-Dihydroxybenzoic acid



4-Hydroxyacetophenone
(p-Hydroxyacetophenone)



Methyl 3-chloro-4-hydroxybenzoate

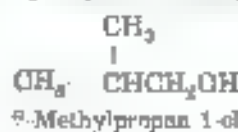
ISOMERISM IN ALCOHOLS

Alcohols exhibit four types of structural isomers.

Chain isomers. Alcohols containing four or more carbon atoms exhibit chain isomerism in which the isomers differ in the chain of carbon atoms attached to the hydroxyl group. For example,

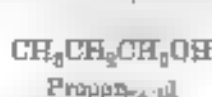


Butan-1-ol

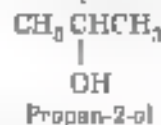


2-Methylpropan-1-ol

Position isomerism. The alcohols containing three or more carbon atoms exhibit position isomerism in which the isomers differ in the position of hydroxyl group. For example,

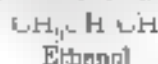


Propan-1-ol

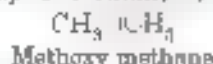


Propan-2-ol

Functional isomerism. Monohydric alcohols containing two or more carbon atoms exhibit functional isomerism in which the isomers differ in the functional group. For example,



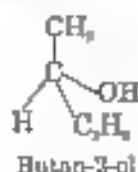
Ethanol



Methoxy methane

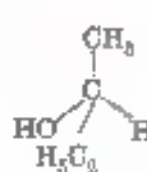
Optical isomerism. Monohydric alcohols containing chiral carbon atoms exhibit optical isomerism.

For example,



Butan-2-ol

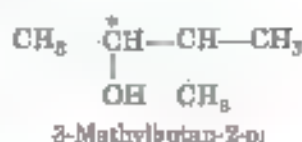
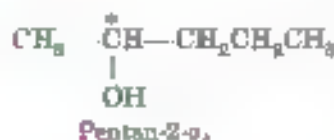
Mirror



REMEMBER

Alcohols and ethers are functional isomers.

Other monohydric alcohols showing optical isomerism are

**HELP**

Check if the compound has chiral carbon atom.

SOLVED EXAMPLES**Example 1**

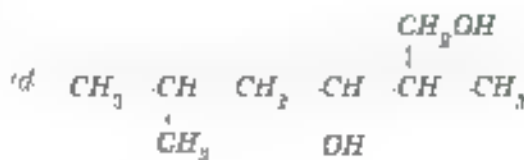
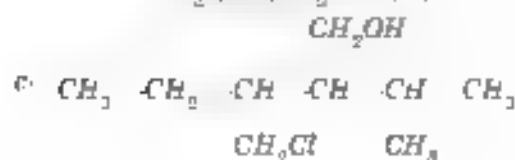
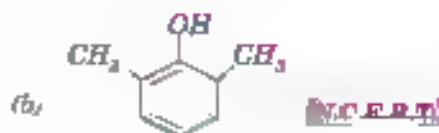
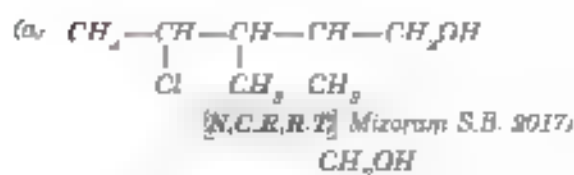
Draw the structures of all isomeric monohydric alcohols of molecular formula $\text{C}_5\text{H}_{12}\text{O}$ and give their IUPAC names. Classify them as primary, secondary and tertiary alcohols. [N.C.E.R.T.]

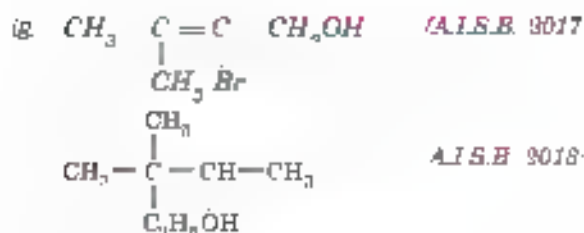
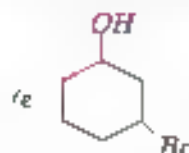
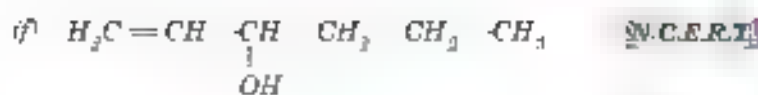
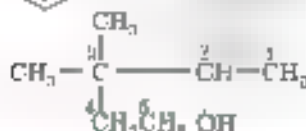
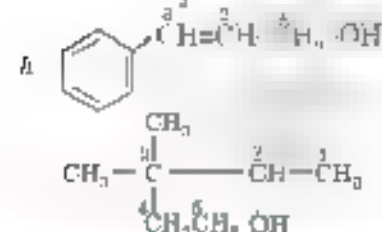
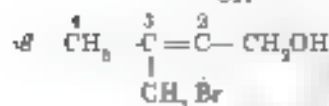
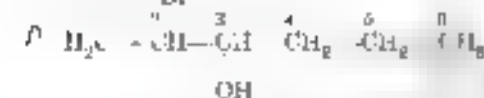
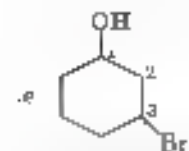
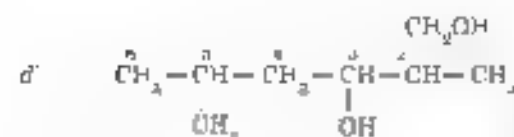
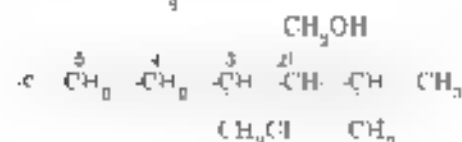
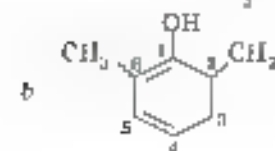
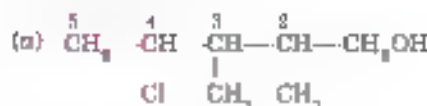
Solution: The isomeric alcohols of molecular formula $\text{C}_5\text{H}_{12}\text{O}$ are

(i) $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$	1. Pentan-1-ol	Primary
(ii) $\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3\text{CH}_2\text{CH}(\text{CH}_2\text{CH}_3)\text{OH} \end{array}$	2-Methylbutan-1-ol	Primary
(iii) $\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3\text{CHCH}_2\text{CH}_2\text{OH} \end{array}$	3-Methylbutan-1-ol	Primary
(iv) $\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3\text{C}(\text{OH})(\text{CH}_3)\text{CH}_2\text{CH}_3 \end{array}$	2, 2-Dimethylpropan-1-ol	Primary
(v) $\begin{array}{c} \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}(\text{OH})\text{CH}_3 \\ \\ \text{OH} \end{array}$	Pentan-2-ol	Secondary
(vi) $\begin{array}{c} \text{CH}_3\text{CH}_2\text{CH}(\text{OH})\text{CH}_2\text{CH}_3 \\ \\ \text{OH} \end{array}$	Pentan-3-ol	Secondary
(vii) $\begin{array}{c} \text{CH}_3\text{CH}(\text{OH})\text{CH}(\text{CH}_3)\text{CH}_2\text{CH}_3 \\ \quad \\ \text{CH}_3 \quad \text{OH} \end{array}$	3-Methylbutan-2-ol	Secondary
(viii) $\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3\text{CH}_2\text{C}(\text{OH})(\text{CH}_3)\text{CH}_3 \\ \\ \text{CH}_3 \end{array}$	2-Methylbutan-2-ol	Tertiary

Example 2

Name the following compounds according to IUPAC system



**Solution:****HELP**

The functional group -OH gets lowest number

4-Chloro-2,3-dimethylpentan-3-ol

2,6-Dimethylphenol

3-Chloromethyl-2-isopropylpentan-1-ol

2,6-Dimethylhexan-1,2-diol

1-Bromocyclohexanol

Hex-1-en-3-ol

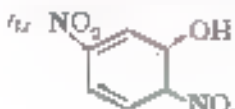
2-Bromo-3-methylbut-2-en-1-ol

3-Phenylprop-2-en-1-ol

3,3-Dimethylpentan-2-ol

Practice Problems

1. Write the IUPAC name of the following compounds.



D.S.B. 2015

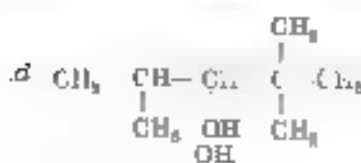


A.I.S.B. 2015



• Ans. (i) 2-Phenylpropen-1-ol
(ii) 1-Phenylpropen-3-ol

2. Give IUPAC names of the following compounds



• Ans. (a) 3-Ethylheptane-2,4-diol

(b) 2,3,4-Trimethylpentan-2-ol

(c) 2-(1-fluoroethyl)butan-2-ol

(d) 5-fluoro-2,4-dihydroxybenzaldehyde

3. Write the formulae of the following alcohols and classify them as 1° or 2°

(a) neo-pentyl alcohol

(b) isobutyl alcohol

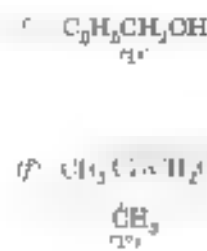
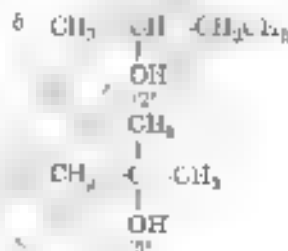
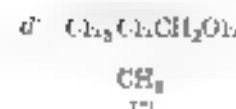
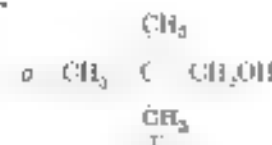
(c) sec-butyl alcohol

(d) tert-butyl alcohol

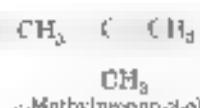
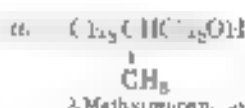
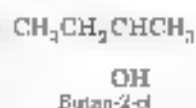
(e) benzyl alcohol

(f) isopentyl alcohol

• Ans.



4. Write all the isomeric alcohols with molecular formula $\text{C}_4\text{H}_{10}\text{O}$ and give their IUPAC names



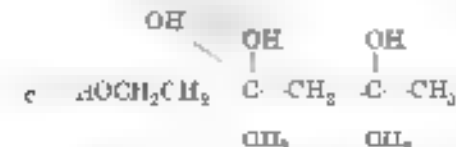
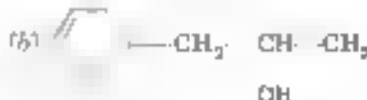
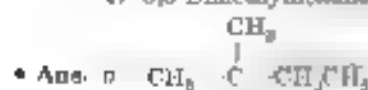
5. Write structures of the compounds whose IUPAC names are given below

(a) 2-Methylbutan-2-ol

(b) 1-Phenylpropan-2-ol

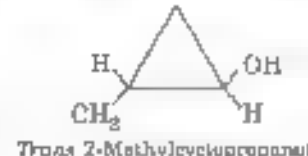
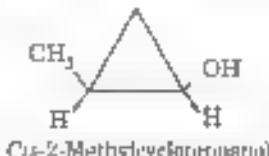
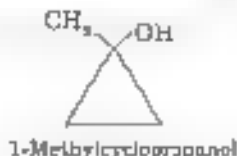
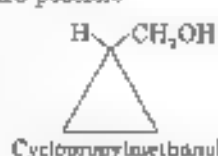
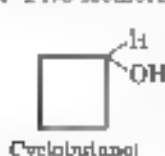
(c) 3,5-Dimethylhexane-1,3,5-triol

(d) Cyclohexyl methanol



6. Give structures of all the cyclic isomers (alcohols) with molecular formula $\text{C}_4\text{H}_8\text{O}$. Write their IUPAC names

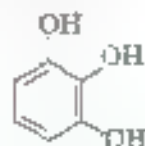
• Ans. Five isomers are possible



7. Write the IUPAC names and draw structures of the following compounds whose common names are given.

(i) Pyrogallol

• Ans. (i)



Benzene-1, 2, 3-triol

(ii) Glycerol

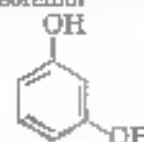
(iii)



Propane-1, 2, 3-triol

(iii) Resorcinol

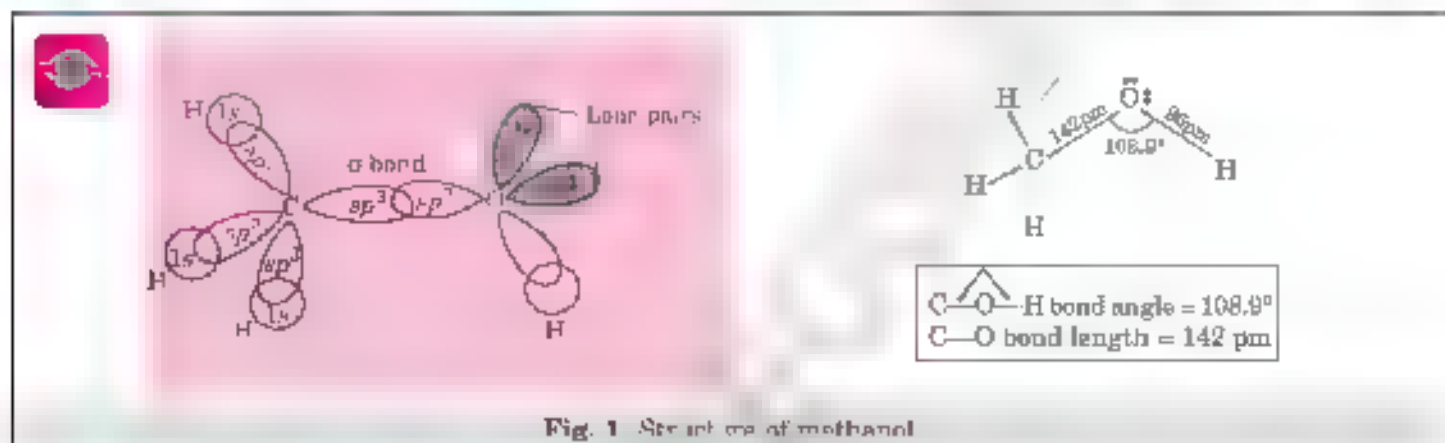
(iii)



Benzene-1, 3-diol

STRUCTURE OF COMPOUNDS CONTAINING —OH GROUP

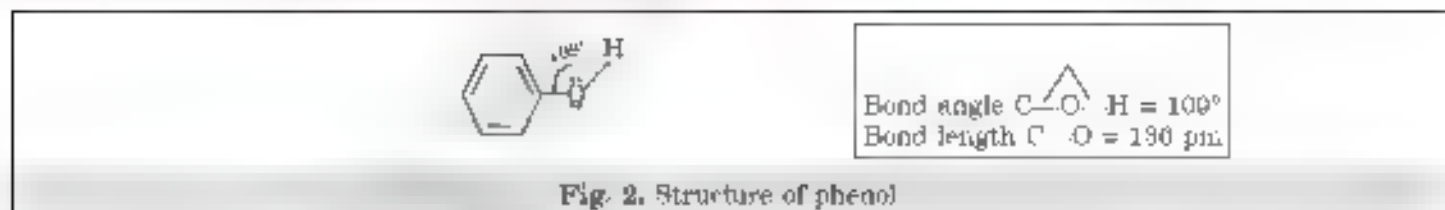
In alcohols, the oxygen of —OH group is bonded to the sp^3 hybridised carbon by a sigma bond. This bond is formed by the overlap of sp^3 hybrid orbital of carbon with one sp^3 hybrid orbital of oxygen. The remaining three sp^3 hybrid orbitals of carbon overlap with 1s orbitals of hydrogen. In the case of oxygen, one sp^3 hybrid orbital overlaps with 1s orbital of hydrogen and the remaining two sp^3 hybrid orbitals contain lone pairs of electrons as shown below for methanol.



The bond angle C—O—H in methanol is slightly less than the tetrahedral angle ($109^\circ 28'$). This is due to larger repulsions between the lone pairs of oxygen.

In contrast to methanol, the —OH group in phenols is attached to sp^2 hybridised carbon of an aromatic ring.

The bond angle C—O—H in phenol is 109° . The C—O bond length 136 pm in phenol is slightly less than that in methanol. This is due to partial double bond character of C—O bond because of the conjugation of lone pair of electrons of oxygen with the aromatic ring.



It may be noted that since the oxygen atom is more electronegative than both carbon and hydrogen, the electrons of C—O and O—H bonds are more displaced towards the O atom. As a result, the electron density near the O atom is slightly more than that near carbon and hydrogen atoms. Consequently an alcohol molecule is dipolar in nature with oxygen carrying a partial negative charge (δ^-) and carbon and hydrogen each carrying a partial positive charge (δ^+). This is supported by the fact that alcohols have high dipole moments. For example, methanol has a dipole moment of 1.71 D.



$$\mu = 1.71 \text{ D}$$

Phenol, on the other hand, has smaller dipole moment, 1.51 D, than methanol. This is due to the reason that C—O bond in phenol is less polar due to electron withdrawing effect of the benzene ring. On the other hand, C—O bond in methanol is more polar due to electron donating effect of the CH_3 group.

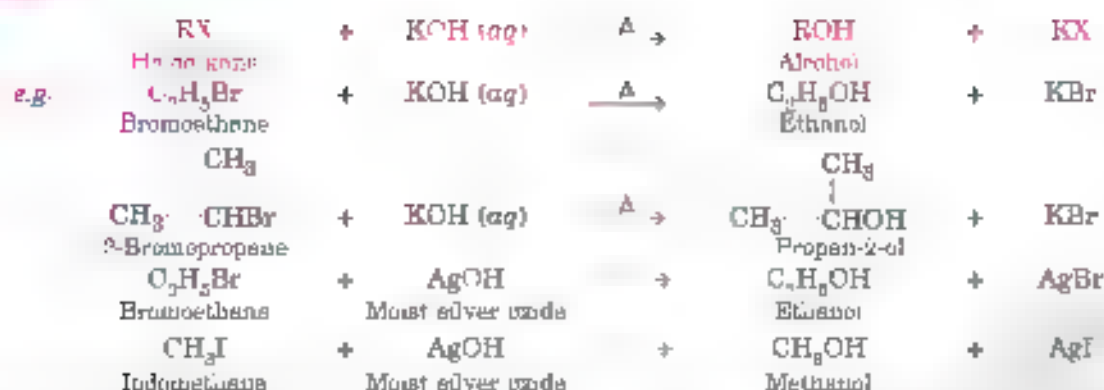
Due to their polar nature, alcohols and phenols form intermolecular hydrogen bonds.

METHODS OF PREPARATION OF ALCOHOLS

The important methods of preparation of alcohols are :

1. Preparation from haloalkanes.

Haloalkanes, when boiled with aqueous NaOH or KOH or moist silver oxide (AgOH) give alcohols.



Primary haloalkanes give good yield of alcohols. However, tertiary haloalkanes on Δ reaction give mainly alkenes due to dehydrohalogenation. Secondary haloalkanes give a mixture of alcohol and alkene.

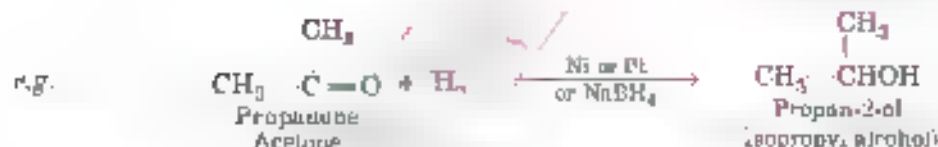
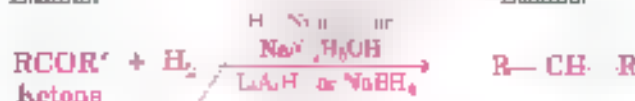
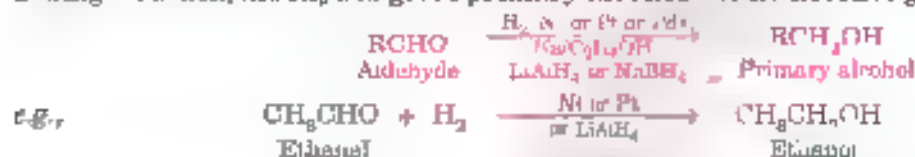


2. By reduction of aldehydes and ketones.

Alcohols are easily prepared by the reduction of aldehydes and ketones.

The reduction is carried out by common reducing agents such as hydrogen in the presence of a catalyst (catalytic hydrogenation) such as finely divided platinum, palladium nickel and ruthenium or sodium in the presence of ethyl alcohol (which in addition to hydride ion also acts by monoauminate III), LiAlH_4 or sodium borohydride (sodium tetrahydrideborate III), NaBH_4 .

During reduction, aldehydes gives primary alcohol while ketones give secondary alcohols. For example,

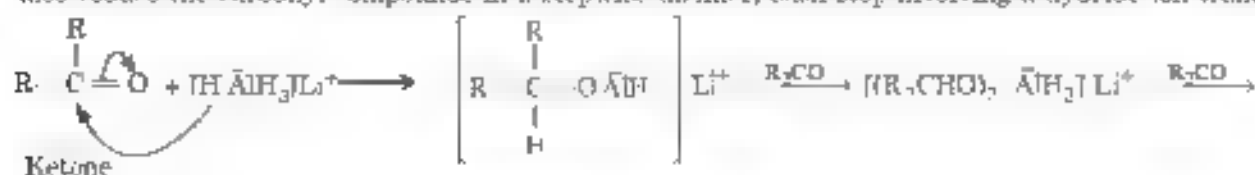


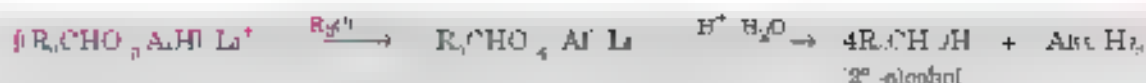
Tertiary alcohols cannot be obtained by reduction of carbonyl compounds.

Reduction of carbonyl compound involves the addition of hydride ion (H^-) reducing the carbonyl group to alkoxide ion which on protonation gives the alcohol.



The complex hydrides LiAlH_4 and NaBH_4 also reduce carbonyl compounds in excellent yields. They also reduce the carbonyl compounds in a stepwise manner, each step involving a hydride ion transfer as





Sodium borohydride ($Na^+ BH_4^-$) also reacts in a similar manner.

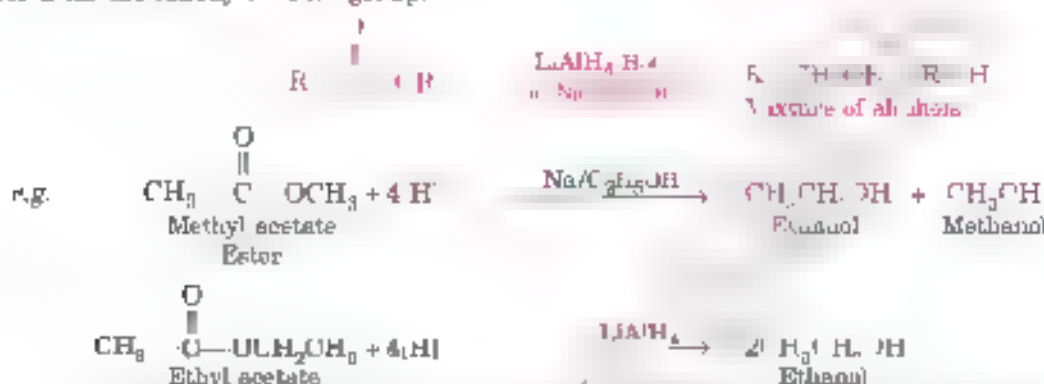
It may be noted that $LiAlH_4$ reacts violently with water and therefore, the reaction with $LiAlH_4$ must be carried out in anhydrous conditions generally in anhydrous ether. Usually ethyl acetate is added cautiously after the reaction is over to decompose excess $LiAlH_4$ and then water is added to decompose aluminium ethoxide.

3. By reduction of carboxylic acids and esters

Carboxylic acids are reduced to primary alcohols in the presence of strong reducing agent, lithium aluminium hydride.

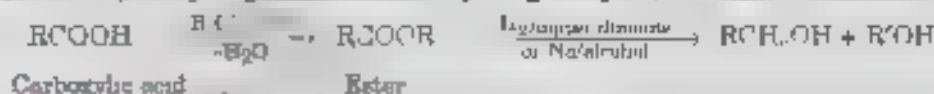


Esters are also reduced to alcohols and give a mixture of two alcohols, one from the acyl group $RCO-$ and the other from the alkoxy ($-OR'$) group.



Reduction of aldehydes, ketones and esters with sodium and alcohol is commonly known as **Bouveault Blanc reduction**.

Note. It may be noted that reduction of carboxylic acids by $LiAlH_4$ gives excellent yield of alcohols. However, $LiAlH_4$ being an expensive reagent, is used only for preparing special chemicals. Therefore, commercially acids are reduced to alcohols by first converting them to the esters followed by their reduction using a hydrogen of the presence of a catalyst (hydrogenation called **hydrogenolysis**) and sodium and alcohol.



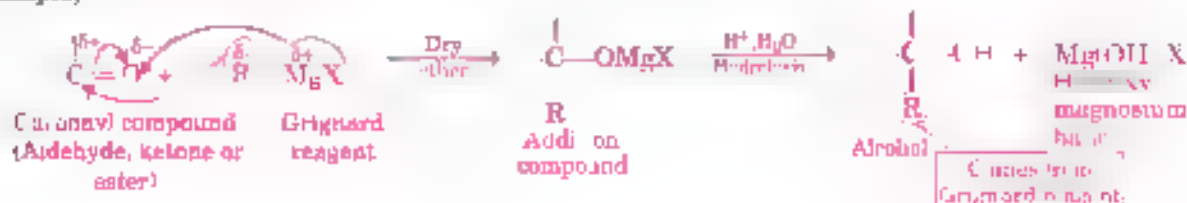
4. From Grignard's reagent

(a) By reaction with aldehydes, ketones and esters

Grignard's reagent $RMgX$ are alkyl or aryl magnesium halides. The $C-Mg$ bond in Grignard's reagent $R-Mg^{\delta+}X^{\delta-}$ is highly polar because carbon is electronegative (electronegativity = 2.5) relative to electropositive magnesium (electronegativity = 1.2). Due to the polar nature of $C-Mg$ bond, Grignard's reagents are very versatile reagents in organic synthesis. Grignard's reagent $RMgX$ reacts with aldehydes, ketones and esters to form addition products which decompose with dil. HCl or dil. H_2SO_4 to give alcohols.

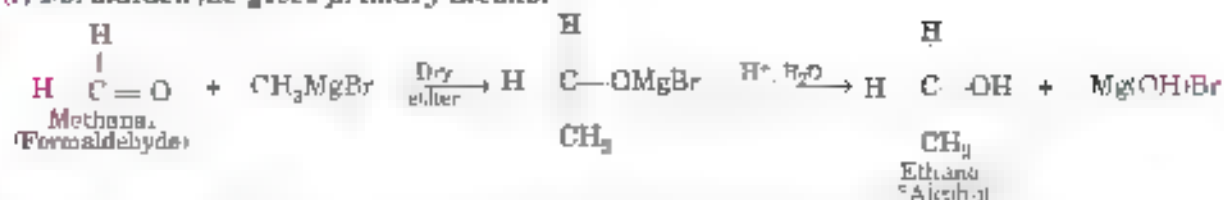
The reaction mechanism involves the simultaneous attack of the nucleophilic alkyl carbanion (R^-) of the Grignard reagent on the carbonyl carbon atom and the remaining portion gets attached to the oxygen atom of carbonyl group forming addition product. This is then decomposed by water to give alcohol.

For example,

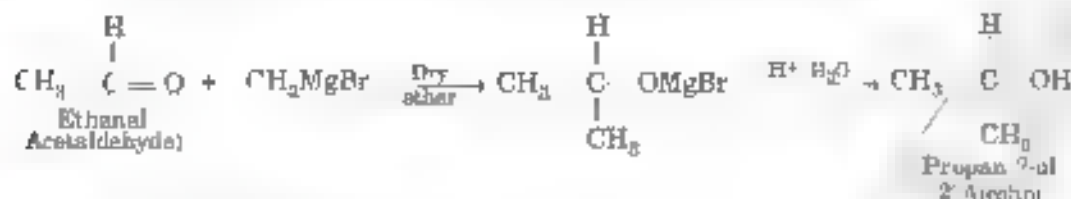


Different types of alcohols are obtained by this reaction

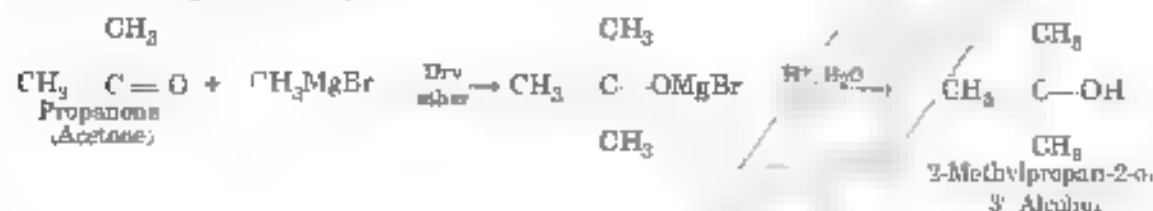
(i) *Formaldehyde gives primary alcohol*



(ii) *All aldehydes (other than formaldehyde) give secondary alcohols*

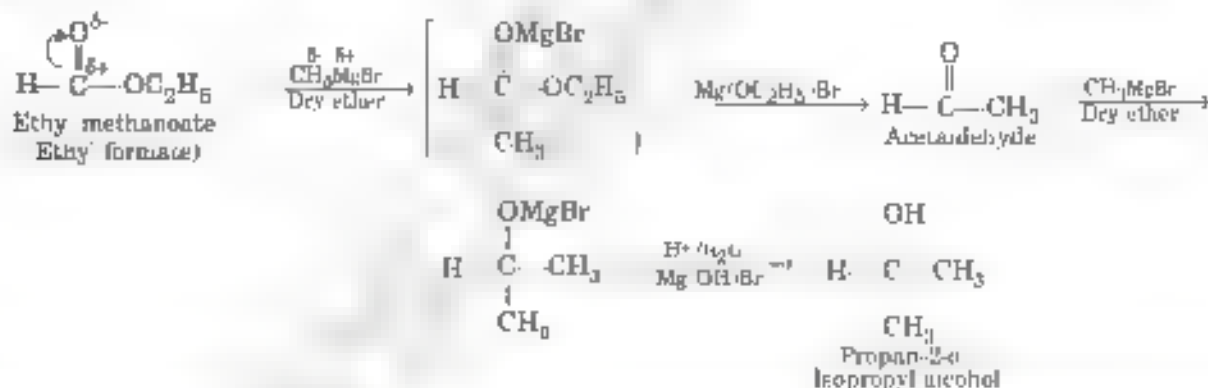


(iii) *Ketones give tertiary alcohols*

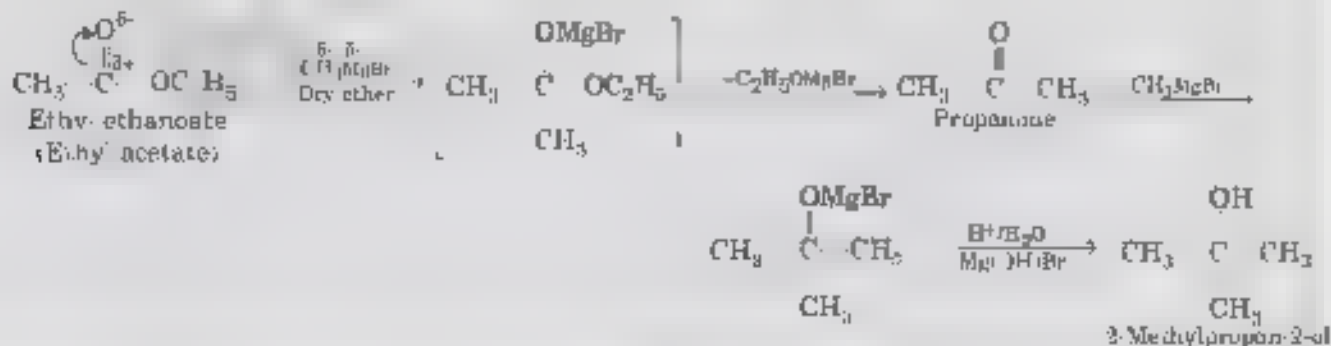


(iv) *Esters give secondary and tertiary alcohols*

Esters can also be converted into alcohols by treating with suitable Grignard reagent. Secondary alcohols can be prepared by the addition of suitable Grignard reagent to esters of formic acid followed by acid hydrolysis. For example,

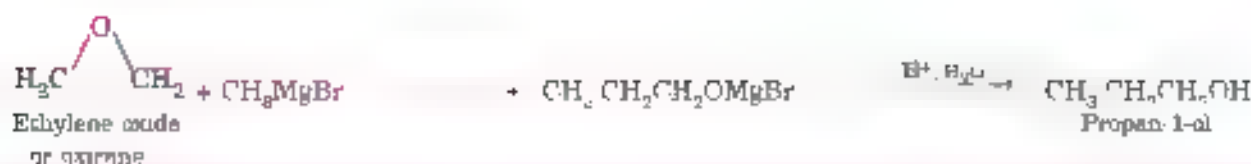


Tertiary alcohols containing at least two identical groups can be easily prepared by the addition of Grignard reagent to an ester other than formic ester followed by acid hydrolysis. For example,

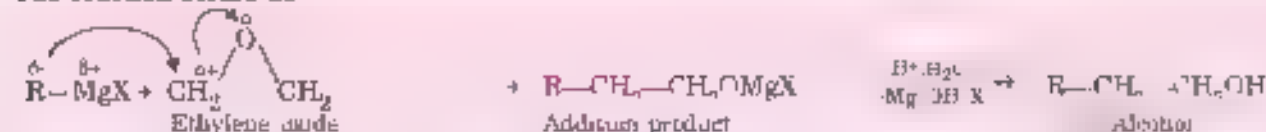


(b) *By reaction with ethylene oxide or oxirane*

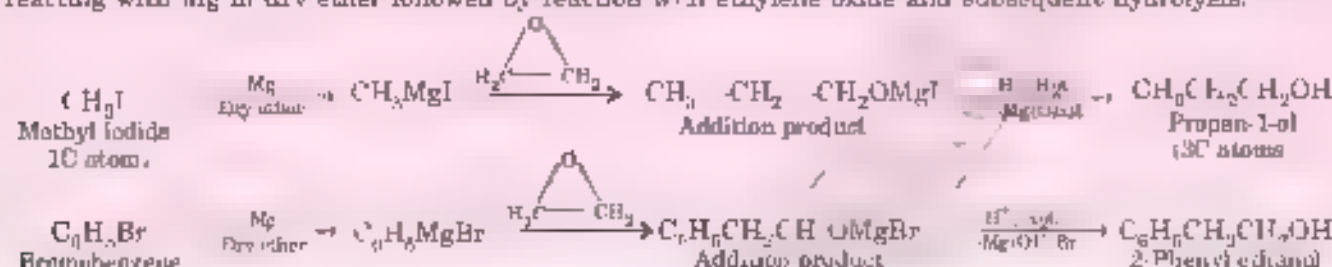
Epoxyalkanes such as oxiranes or ethylene oxide react with Grignard reagent in the presence of anhydrous ether to form addition products which are hydrolysed by water in the presence of acid to form alcohols. For example



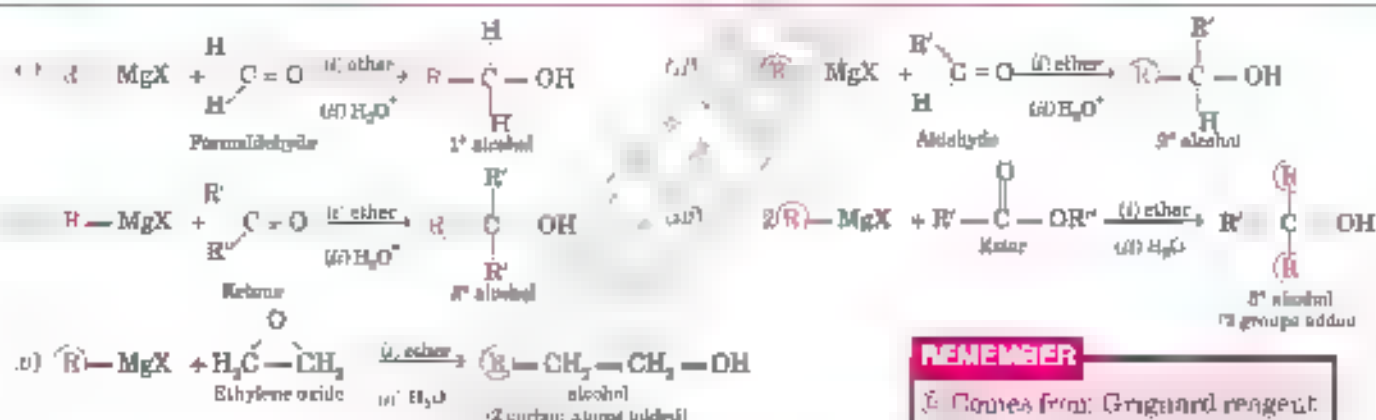
The reaction occurs as



This is an excellent method for converting an alkyl halide into a **primary alcohol containing two carbon atoms more than the alkyl halide**. The alkyl halide is first converted into the corresponding Grignard reagent by reacting with Mg in dry ether followed by reaction with ethylene oxide and subsequent hydrolysis.



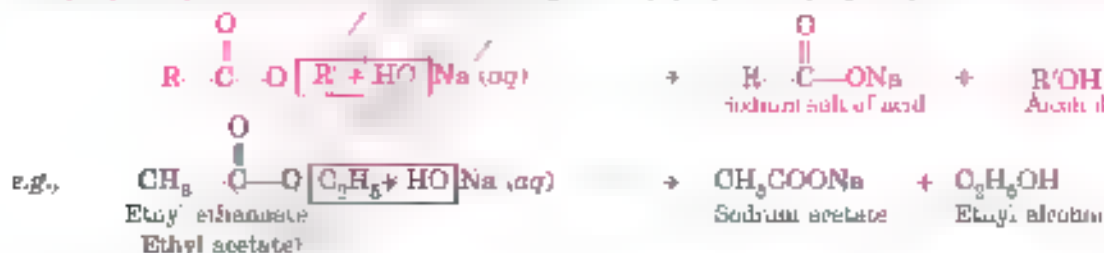
Summary : Grignard Reagent for Preparing Alcohols



REMEMBER

1. Comes from Grignard reagent.

5. **By hydrolysis of esters.** Alcohols are generally prepared by hydrolysis of esters with aqueous alkalis.



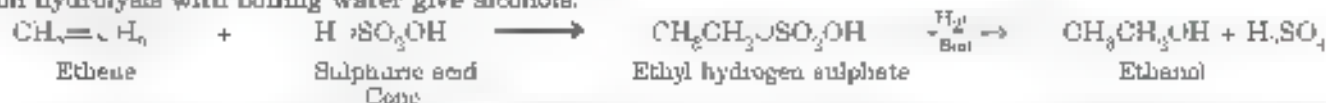
6. From alkenes.

Alkenes can be converted into alcohols by the following methods

(a) By acid catalysed hydration of alkenes

The hydration of alkenes can be carried out directly or indirectly

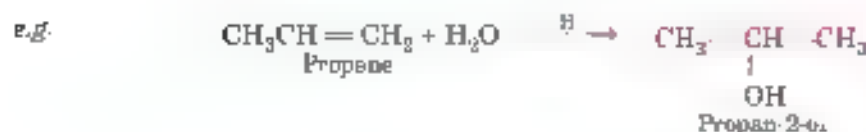
In the **indirect process**, alkenes are passed through conc H_2SO_4 to form alkyl hydrogen sulphates, which upon hydrolysis with boiling water give alcohols.



In case of unsymmetrical alkenes, the addition of H_2SO_4 takes place in accordance with **Markovnikov's rule** i.e. Hydrogen goes to that carbon atom which contains large number of hydrogen atoms.



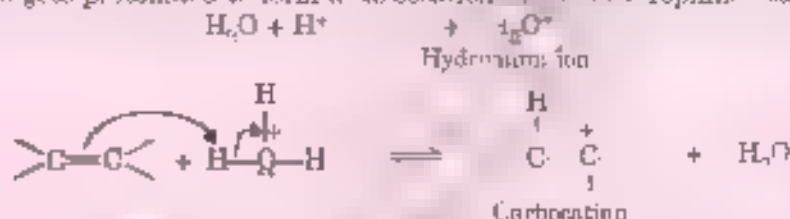
Reactive alkenes directly add a molecule of water in the presence of mineral acids as catalyst to form an alcohol.



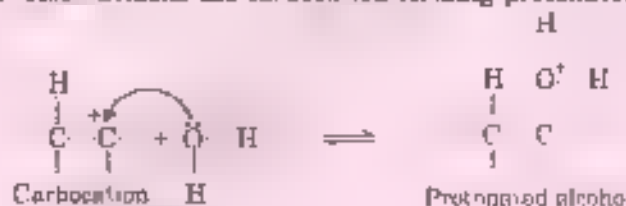
MECHANISM: Hydration of alkenes

The mechanism of the reaction involves the following steps:

Step 1: Alkene gets protonated to form a carbocation \rightarrow electrophilic attack of H_3O^+



Step 2: Nucleophile (H_2O) attacks the carbocation forming protonated alcohol



Step 3: Loss of H^+ from oxygen (deprotonation) to form alcohol



NOTE

It may be noted that during step 1, addition of a proton occurs on that carbon atom of the double bond which gives a more stable carbocation.

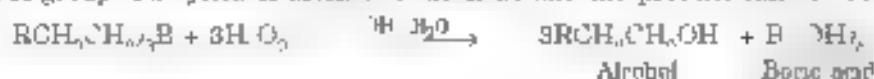
(b) Hydroboration oxidation reduction. Alkenes react with diborane B_2H_6 to form trialkyl boranes which upon subsequent treatment with alkaline H_2O_2 give alcohols. This reaction involves the addition of water to a double bond opposite to that of Markovnikov's rule i.e. **anti-Markovnikov's rule**. This involves two reactions, addition of borane BH_3 to double bond called **hydroboration-oxidation** and **hydrolysis** to give an alcohol.



Diborane is an electron deficient molecule. Therefore, it acts as an electrophile reacting with alkene to form alkyl boranes R_2B as



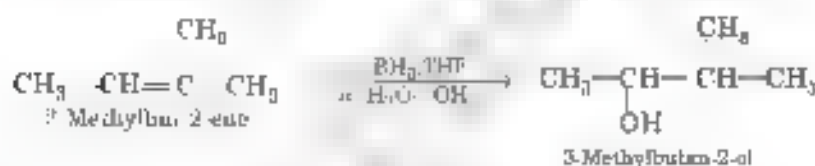
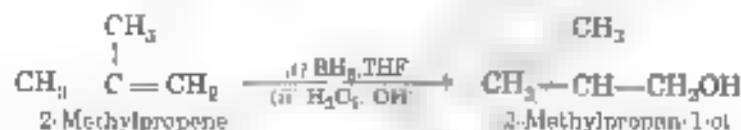
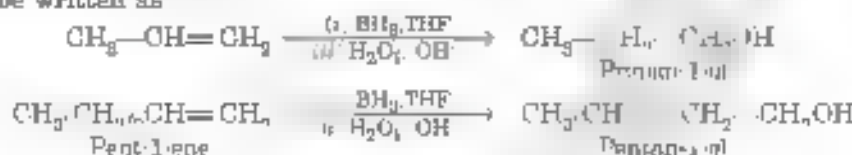
In each addition step, the boron atom is attached to carbon atom of the double bond that is bonded to larger number of hydrogen atoms. The hydrogen atom is transferred from boron atom to the other carbon atom of the double bond. Thus, the addition occurs according to **anti-Markovnikov's rule**. During oxidation of trialkyl borane, boron is replaced by -OH group. The yield of alcohol is excellent and the product can be easily isolated.



e.g.,



or the reaction may be written as



(c) Oxymercuration-demercuration reaction

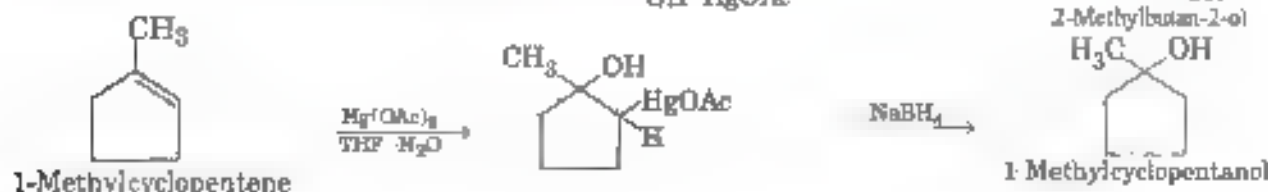
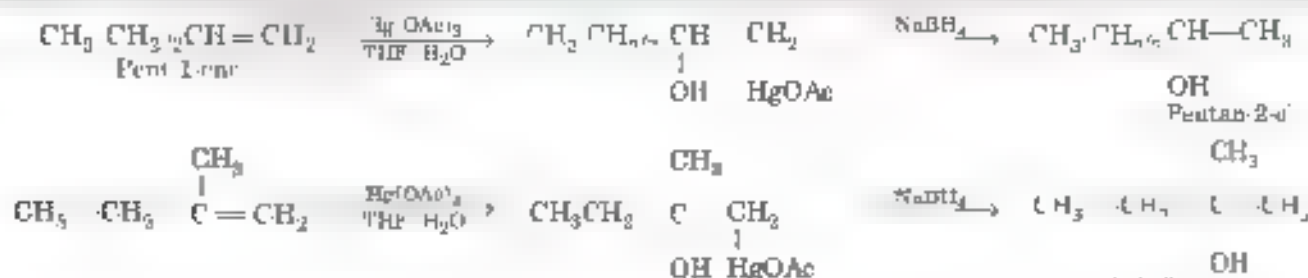
Alkenes react with mercuric acetate ($\text{CH}_3\text{COO})_2\text{Hg}$ or $\text{Hg}(\text{OAc})_2$ in the presence of water to form oxymercuration adducts which, upon reduction with NaBH_4 in a basic medium give alcohols.

Alkenes react with mercuric acetate in a mixture of tetrahydrofuran (THF) and water to give hydroxyalkyl mercury compound involving addition of $\text{CH}_3\text{COO}-\text{Hg}-\text{OAc}$ to the double bond. This is called **oxymercuration**. In the second step, sodium borohydride reduces $-\text{Hg}-\text{OAc}$ and replaces it with hydrogen. This is called **demercuration**.



The net reaction involves addition of H and OH in accordance with **Markovnikov's rule**.

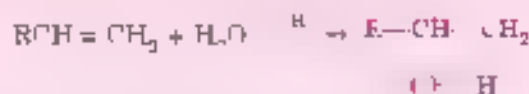
This reaction is very fast and produces the alcohol in high yield. The alcohol obtained corresponds to Markovnikov's addition of water to alkene.



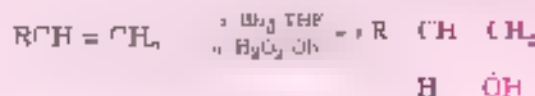
REMEMBER

Alkenes can be converted to alcohols

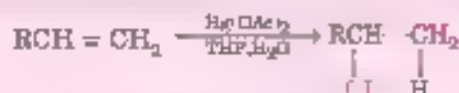
- Acid catalyzed hydration proceeds according to **Markovnikov rule**



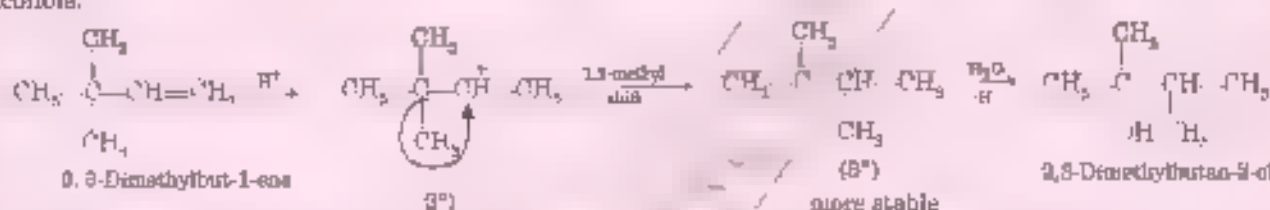
- Hydroboration-oxidation reduction proceeds according to an **anti-Markovnikov rule**



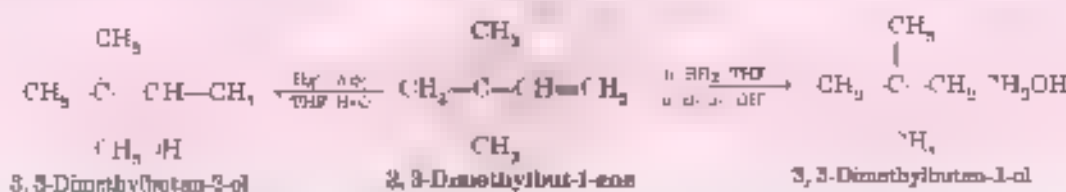
- Oxidation-dehydration proceeds according to **Markovnikov rule**



- Hydration of alkene occurs through carbocation intermediates. Since carbocations have a tendency to undergo rearrangement to form stable carbocations (by 1,2-hydride shift or 1,2-methyl shift), the products are rearranged alcohols.

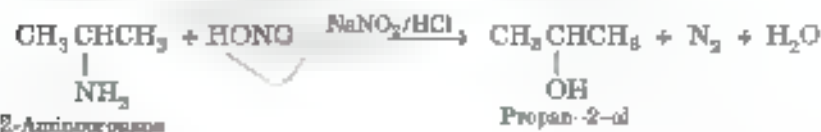
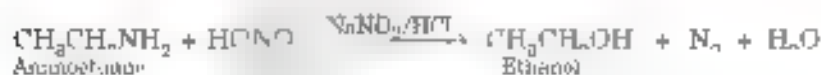
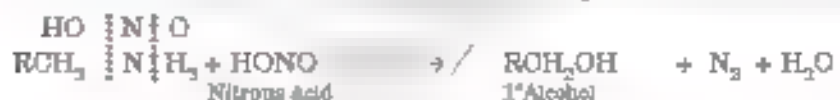


- Hydroboration-oxidation or oxymercuration followed with anti-Markovnikov reagents must involve carbocation intermediates and hence always form expected (unrearranged) alcohols.



8. From aliphatic primary amines

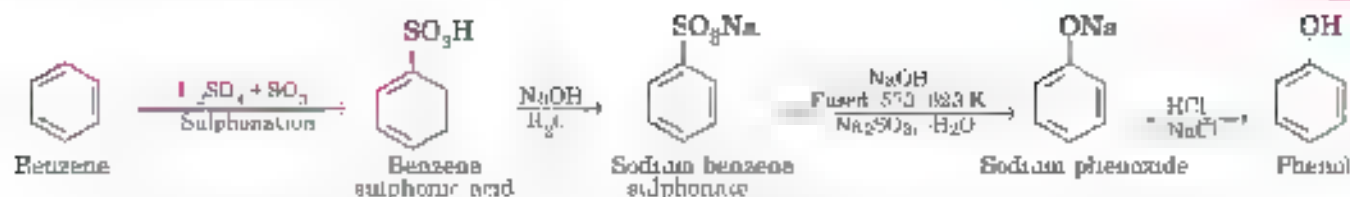
Primary amines react with nitrous acid (HNO_2) to form alcohols along with the evolution of nitrogen gas



METHODS OF PREPARATION OF PHENOLS

Phenol is a so called **carboic acid**. It was first isolated in the early 19th century from coal tar. Nowadays, phenol is manufactured synthetically. In the laboratory, phenols are prepared from benzene derivatives by the following methods:

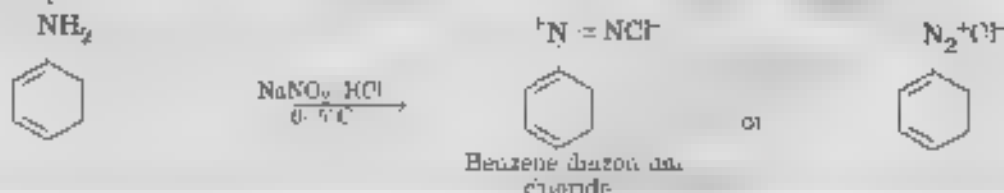
1. From benzene sulphonic acid. Benzene is sulphonated with oleum (mixture of H_2SO_4 and SO_3 or $\text{H}_2\text{S}_2\text{O}_7$) and benzene sulphonic acid so formed is converted to sodium phenoxide by heating with molten sodium hydroxide. This on acidification gives phenol.



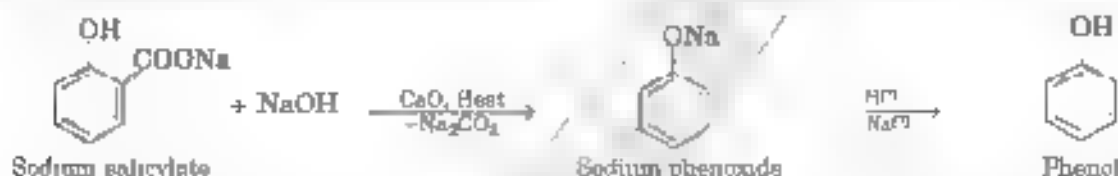
2. From diazonium salts. An aqueous solution of benzene diazonium salt on warming gives phenol.



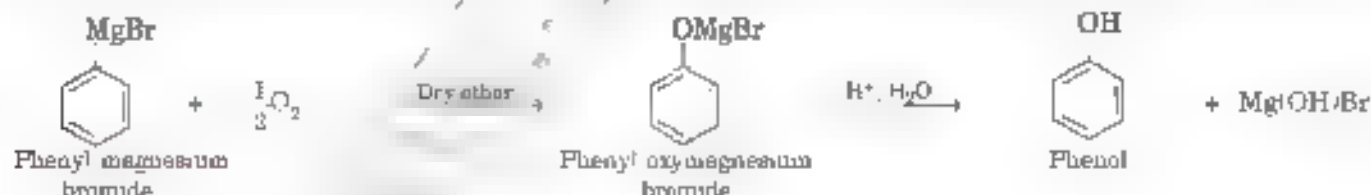
Benzene diazonium chloride required for the reaction is obtained by treating benzene with nitrous acid (HNO_2) + HCl at low temperature 278-278 K ($0-5^\circ\text{C}$). This reaction is called **diazotisation reaction**.



3. By decarboxylation of sodium salt of salicylic acid. Phenol can be prepared by fusing sodium salicylate with soda lime (NaOH and CaO mixture) followed by acidification with dil. HCl .



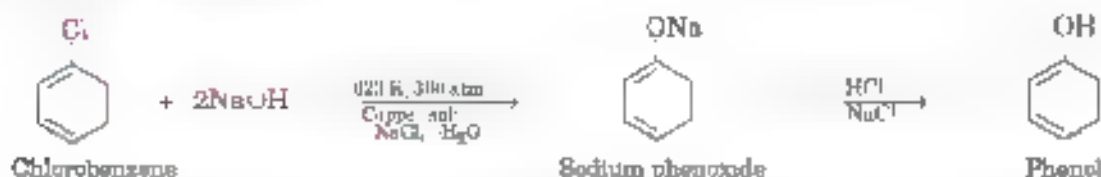
4. From Grignard reagent. When oxygen gas is bubbled through an ethereal solution of phenyl magnesium bromide (Grignard reagent), it forms an oxy compound which upon hydrolysis with dilute mineral acid gives phenol.



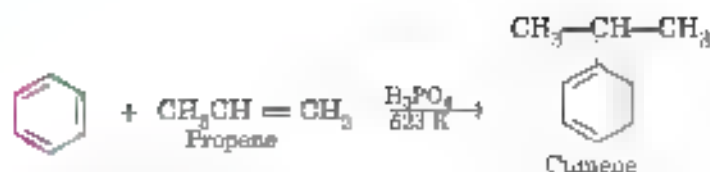
Commercial Preparation of Phenols

On a large scale, phenol is obtained by the following methods

1. From chlorobenzene (Dow's process). Phenol is manufactured by heating chlorobenzene with 10% aqueous sodium hydroxide solution at about 623 K under 800 atmospheres and in the presence of copper salt acting as catalyst to form sodium phenoxide. The sodium salt when treated with dilute HCl , gives phenol. This method is called **Dow's process**.

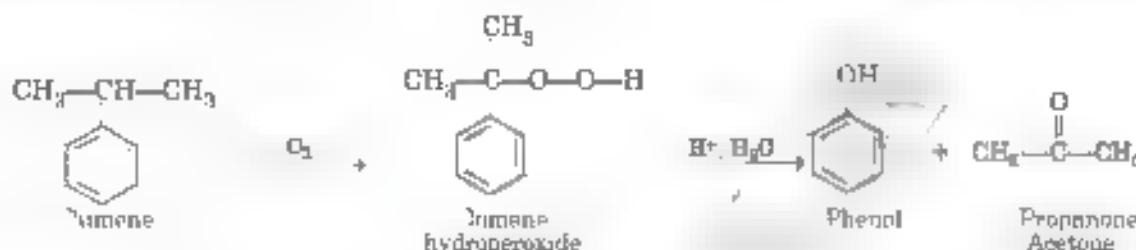


2. From cumene. Phenol is prepared commercially from cumene (isopropyl benzene). Cumene is prepared by Friedel-Crafts alkylation of benzene with propene in the presence of phosphoric acid at 623 K.

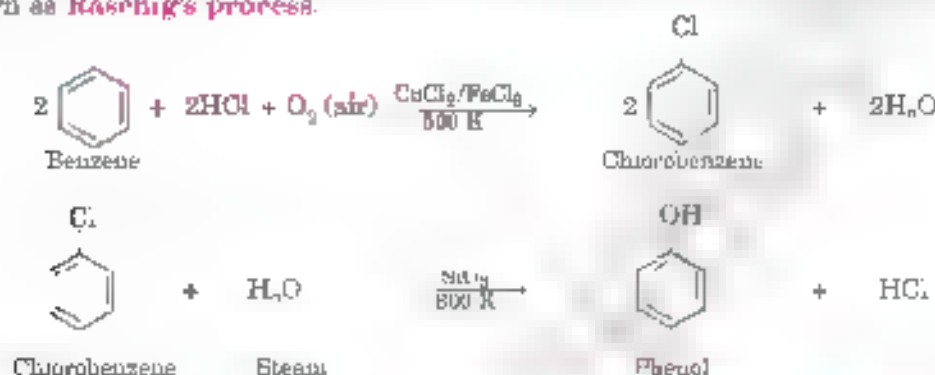


This reaction is Friedel Crafts alkylation reaction.

Cumene is oxidised in the presence of air to cumene hydroperoxide which upon subsequent hydrolysis with dil. H_2SO_4 gives phenol and propanone (acetone).



3. From benzene (Raschig's method). Vapours of hydrochloric acid are passed over benzene at 500 K in the presence of copper (II) chloride catalyst and ferric chloride catalyst and excess of air to form chlorobenzene. Steam is then passed through chlorobenzene at 800 K in the presence of sodium as catalyst to give phenol. This method is known as **Raschig's process**.



SOME EXAMPLES

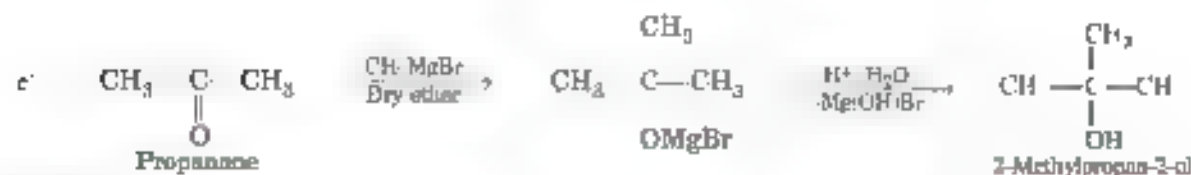
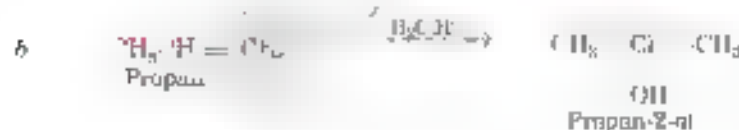
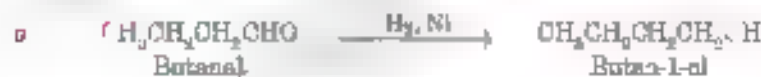
□ Example 3.

Give the structures and IUPAC names of products expected from the following reactions

- Catalytic reduction of butanal
- Hydration of propene in the presence of dilute sulphuric acid.
- Reaction of propanone with methyl magnesium bromide followed by hydrolysis

[N.C.E.R.T.]

Soln. (a)



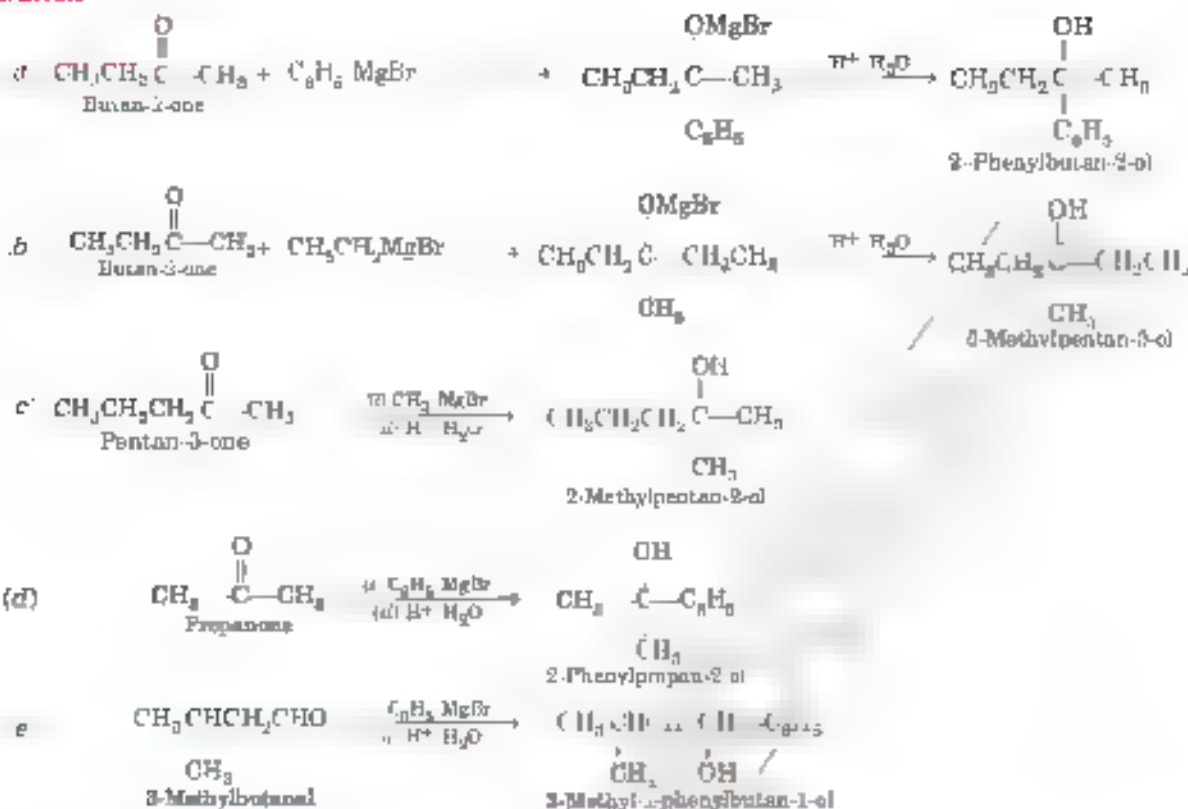
□ Example 4.

Use a Grignard's reagent to prepare the following alcohols

- 2-Phenylbutan-2-ol
- 3-Methylpentan-3-ol
- 2-Methylpentan-2-ol
- 2-Phenylpropan-2-ol

(c) 3-Methyl 1-phenylbutan-1-ol.

Solution



PHYSICAL PROPERTIES OF ALCOHOLS

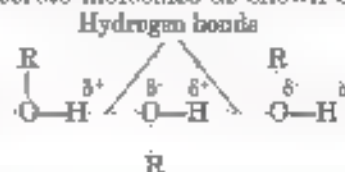
The important physical properties of alcohols are

(i) **Physical state.** At ordinary temperature the lower members are colourless liquids having a characteristic smell and burning taste. The higher members (having more than 12 carbon atoms) are colourless, odourless, wax-like solids.

(ii) **Boiling points.** The boiling points of alcohols are much higher than the corresponding aliphatic hydrocarbons and haloalkanes. For example,

Compound	CH_4	CH_3Cl	CH_3Br	CH_3OH
Boiling point	90 K	249 K	278 K	357.5 K

This is because there is large difference in electronegativities of oxygen and hydrogen atoms. As a result, the O—H bond is strongly polar and forms hydrogen bonds in alcohols. Because of hydrogen bonds in alcohols, these exist as associated molecules rather than discrete molecules as shown below.



Therefore, a large amount of energy is needed to break these extensive hydrogen bonds and hence their boiling points are high.

It may be noted that alcohols have generally higher boiling points as compared to their isomeric ethers of same molecular masses. For example, the boiling point of ethyl alcohol (mol. mass = 46), dimethyl ether (mol. mass = 46), and propane (mol. mass = 44) are

Ethyl alcohol	Dimethyl ether	Propane
351 K	248 K	231 K

This is due to the presence of intermolecular hydrogen bonds in alcohols and their absence in ethers and hydrocarbons.

The lower members have low boiling points but, with the increase in number of carbon atoms (molecular mass), the boiling points keep on increasing gradually. This is because of increase in van der Waals forces. For isomeric alcohols having the same number of carbon atoms, the boiling points are in the order

primary > secondary > tertiary.

Compound	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$ Butan-1-ol (1°)	$\text{CH}_3\text{CH}(\text{CH}_3)\text{CH}_2\text{OH}$ 2-Methylpropan-1-ol (1°)	$\text{CH}_3\text{CH}_2\text{CH}(\text{OH})\text{CH}_3$ Butan-2-ol (2°)	$\text{CH}_3\text{C}(\text{OH})(\text{CH}_3)_2$ 2-Methylpropan-2-ol (3°)
Boiling point	391 K	381 K	379 K	356 K

This is due to the fact that *with branching, the surface area decreases and therefore van der Waals forces decrease. Consequently, boiling point also decreases.*

(iii) Solubility The lower members of alcohols are highly soluble in water but the solubility decreases with increase in molecular weight. The solubility of lower alcohols in water is due to the formation of hydrogen bonds between alcohols and water molecules.

However, as the size of alcohol molecule increases, the alkyl group becomes larger and prevents the formation of hydrogen bonds with water molecules and hence the solubility goes on decreasing with increase in length of carbon chain or molecular mass of alcohol.

For example,

Alcohol Solubility (in g/100g H_2O)	n-Butyl alcohol	n-Pentyl alcohol	n-Hexyl alcohol	n-Heptyl alcohol
	7.9	2.3	0.55	0.2

However, amongst isomeric alcohols, the solubility increases with branching. This is due to the reason that as the branching increases, the surface area of non-polar hydrocarbon part decreases and the solubility increases.

Alcohol Solubility (in g/100g H_2O)	n-Butyl alcohol	Isobutyl alcohol	Sec-butyl alcohol	tert-Butyl alcohol
	7.9	0.0	12.5	very large

(iv) Density Generally, alcohols are lighter than water although the density increases with increase in molecular mass.

(v) Intoxicating effects. Alcohols have intoxicating effects. Methanol is poisonous and is not good for drinking purposes. It may cause blindness and even death. Ethanol is used for drinking purposes.

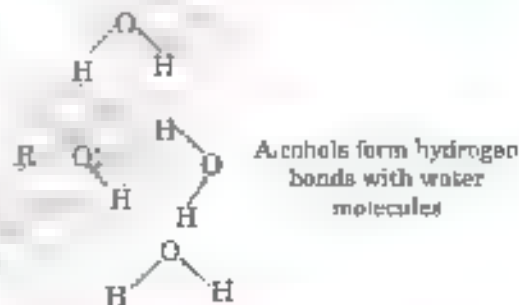
PHYSICAL PROPERTIES OF PHENOLS

The important physical properties of phenol are

- 1. State and smell.** Phenols are colourless crystalline solids or liquids. They have characteristic phenolic odours.
- 2. Solubility.** Unlike alcohols, phenols are sparingly soluble in water. The non-polar aryl group is very large in size and it almost completely masks the polar character of the -OH group. However, phenols are soluble in alcohols, ethers and also in NaOH.
- 3. Boiling points.** The boiling points of phenols are higher than the boiling points of the aromatic hydrocarbons and haloarenes of comparable molecular masses. For example, boiling point of phenol (molecular mass = 94) is 455 K while that of toluene (molecular mass = 92) is 384 K.

Compound	$\text{C}_6\text{H}_5\text{OH}$ Phenol	$\text{C}_6\text{H}_5\text{CH}_3$ Toluene	$\text{C}_6\text{H}_5\text{Cl}$ Chlorobenzene
Boiling point	455 K	384 K	405

The higher boiling point is due to the presence of intermolecular hydrogen bonding in phenols. Therefore, they exist as associated molecules.



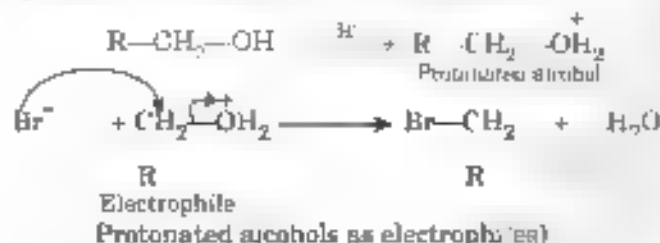
CHEMICAL PROPERTIES OF ALCOHOLS

Alcohols are versatile compounds. They behave both as nucleophiles as well as electrophiles as

a They behave as **nucleophiles** in the reactions in which the bond between $\text{O}-\text{H}$ is broken as shown below



b They behave as **electrophiles** in which the bond between $\text{C}-\text{O}$ is broken. These reactions are carried out in the presence of acids to form protonated alcohols. Protonated alcohols react as electrophiles.



On the basis of cleavage of different bonds, the reactions of alcohols may be divided into the following types

A. Reactions involving cleavage of oxygen-hydrogen bond.

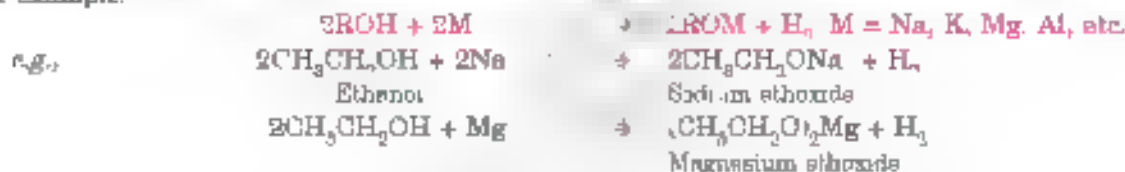
B. Reactions involving cleavage of carbon-oxygen bond

C. Reactions involving both the alkyl and hydroxyl groups

A. Reactions Involving the Cleavage of Oxygen-Hydrogen bond



1. Reaction with active metals—acidic character Alcohols are weakly acidic in nature and react with active metals such as sodium, potassium, magnesium and calcium etc. to liberate hydrogen gas and form metal alkoxide. For example,



The above reaction shows alcohols are **acidic** in nature. The alcohols act as Bronsted acids because they donate a proton to a strong base (B^-). For example,



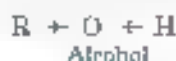
On reacting an alkoxide with water, the starting alcohol is obtained



This reaction shows that **water is a better proton donor than alcohol. In other words, water is stronger acid than alcohols.** We can also note that alkoxide is a better proton acceptor than hydroxide ion. This means **alkoxides are stronger bases than hydroxide ion.** For example sodium ethoxide is a stronger base than sodium hydroxide

The acidic nature of alcohols is due to the presence of polar $\text{O}-\text{H}$ bond. Oxygen is more electronegative than hydrogen and therefore, it withdraws the shared electron pair between O and H atoms towards itself. As a result,

O—H bond becomes weak and loses a proton (H^+). Therefore alcohols behave as acids. However, alcohols are weak acids ($K_a = 10^{-16}$ to 10^{-18}) even weaker than water ($K_a = 1 \times 10^{-14}$). This is quite expected because of the *electron releasing inductive effect* +I effect of the *alkyl group* (H_2). The alkyl group releases electrons towards oxygen atom and increases electron density over the oxygen atom, tending to decrease the polarity of O—H bond. As a result, the tendency of oxygen to withdraw electrons in O—H bond towards itself decreases and therefore, the release of proton (H^+) becomes difficult. On the other hand, there is no electron releasing alkyl group in water and the electron pair of O—H bond gets more attracted towards oxygen atom than in alcohol. Thus, the release of H^+ from water is easier than it is slightly less in alcohol. Thus, **alcohols are weaker acids than water**.



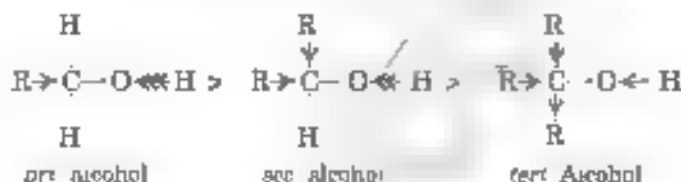
Comparison of acidic strength of different types of alcohols

The order of acidic strength among various types of alcohols is

primary > secondary > tertiary

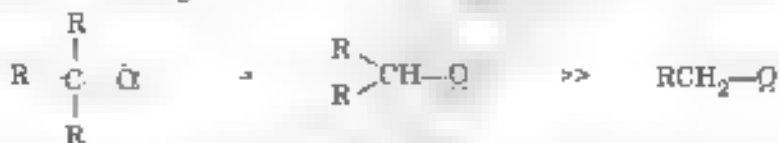
This order can be easily explained in terms of *electron releasing inductive effect of alkyl groups*. The acidic character of alcohols is due to the cleavage of O—H bond giving H^+ .

The alkyl groups are electron releasing groups +I effect and they increase the electron density around the oxygen. As a result, the electrons of O—H bond cannot be withdrawn strongly towards oxygen and O—H remains strong. Therefore, greater is the number of alkyl groups present, smaller will be its tendency to release proton (H^+) and consequently weaker will be its acidic strength. Now, electron releasing effect would be maximum in tertiary alcohols and least in primary alcohols. Thus, the acidic character decreases as

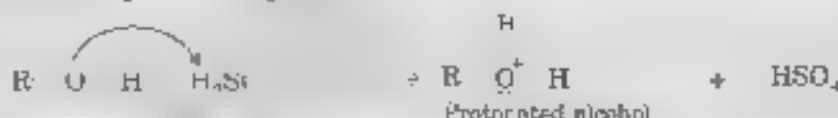


Acidic character decreases 

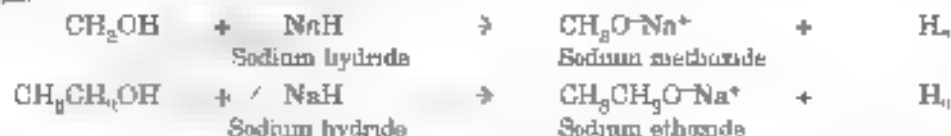
Obviously, the basic strength of their alkoxides follows the reverse order



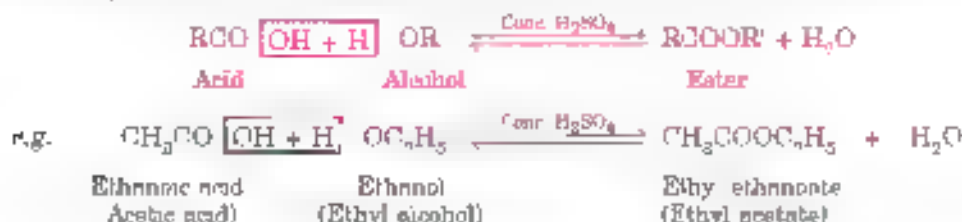
It may be noted that alcohols act as Lewis bases also. This is due to the presence of lone pairs on oxygen which makes alcohols proton acceptors.



2. Reaction with metal hydrides. Alcohols react with metal hydrides to form alkoxides with the evolution of hydrogen gas.

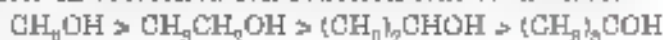


3. Reaction with carboxylic acids (esterification). Alcohols react with monocarboxylic acids, in the presence of conc. H_2SO_4 or dry HCl gas as catalyst, to form esters. The reaction is known as **esterification**. The function of conc. H_2SO_4 is to act as protonating agent as well as a dehydrating agent.



The reaction is reversible in nature and the eq. n. brian can be shifted towards the forward direction by removing water as soon as it is formed. When HCl gas is used as a catalyst, the reaction is called **Fischer-Speier esterification**.

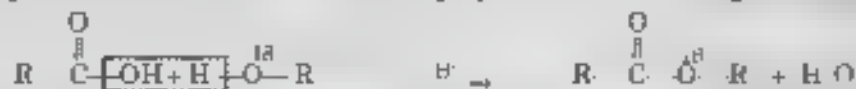
It may be noted that the presence of bulky groups in the alcohol or in the acid decreases the rate of esterification. This is due to *steric hindrance* of bulky groups. As a result, it is difficult to prepare esters of tertiary alcohol. Thus, the order of reactivity of alcohols in esterification reaction follows the order



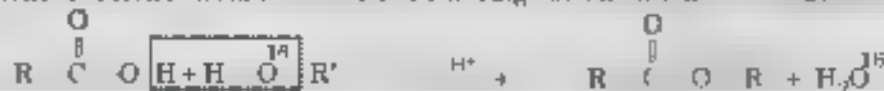
The order of carboxylic acids follows the sequence



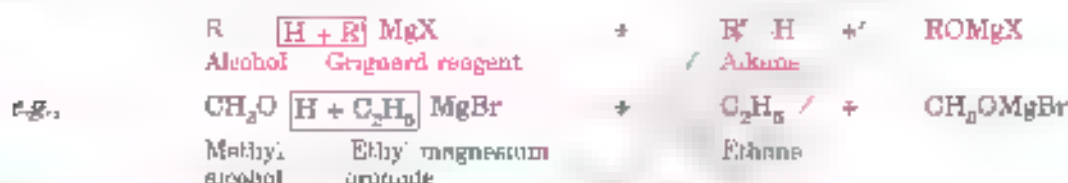
Note : It is important to note that esterification involves the cleavage of the O—H bond of alcohol. This has been established by isotopic tracer technique. If the reaction is carried out with an alcohol having isotopic oxygen O^{18} (which can be easily traced because of its radioactive properties), the resulting ester contains this isotope of oxygen.



If the C—O bond of alcohol would have cleaved during esterification, O^{18} would have gone to resulting water.



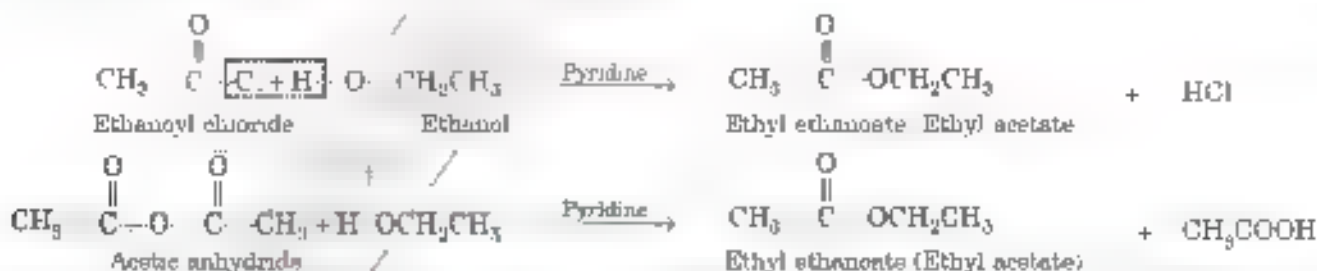
4. Reaction with Grignard reagents. Alcohols react with Grignard reagents which are alkyl magnesium halides, RMgX to form hydrocarbons.



NOTE

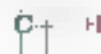
It may be noted that alkane formed corresponds to the alkyl group of the Grignard reagent.

5. Reaction with acyl chloride or acid anhydride (acylation). When alcohols are treated with acid chloride or acid anhydride in the presence of bases like pyridine or dimethyl amine (as catalyst), the hydrogen atom of —OH group is replaced by acyl ($\text{RCO}-$) group forming esters.



This reaction is called **acylation reaction**. If the acid chloride or anhydride used are acetyl chloride and acetic anhydride, the reaction is usually called **acetylation** which means the introduction of acetyl (CH_3CO) group in alcohols. It may be noted that the reaction with acetyl chloride is carried out in the presence of a base pyridine to neutralise HCl which is formed during the reaction. It shifts the eq. n. brian to the forward direction.

B. Reactions Involving Cleavage of Carbon-Oxygen Bond



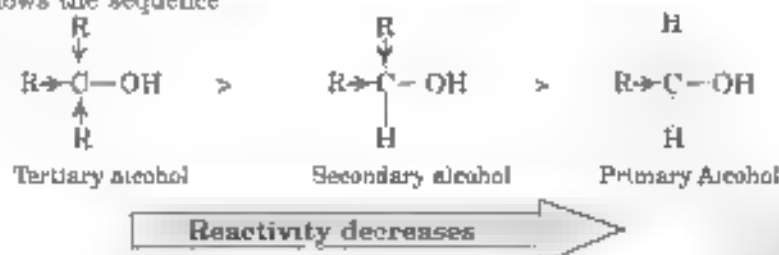
Alcohols undergo a number of reactions involving the cleavage of carbon-oxygen ($\text{C}-\text{OH}$) bond. In these reactions, the order of reactivity of alcohols is

tertiary > secondary > primary

This can be explained in terms of *electron releasing inductive effect of alkyl groups*. The alkyl groups release electrons and, therefore, they increase the electron density towards oxygen. As a result, the polarity of $\text{C}-\text{O}$ bond increases and this makes the cleavage of the bond between carbon and oxygen easier. Therefore, the greater the

number of alkyl groups attached to the carbon. The more easy would be the cleavage of C-O bond and consequently, the greater would be the reactivity of alcohol.

Thus, the reactivity follows the sequence



1. Reaction with hydrogen halides. Alcohols react with hydrogen halides to form haloalkanes (alkyl halides). The order of reactivity of hydrogen halides is

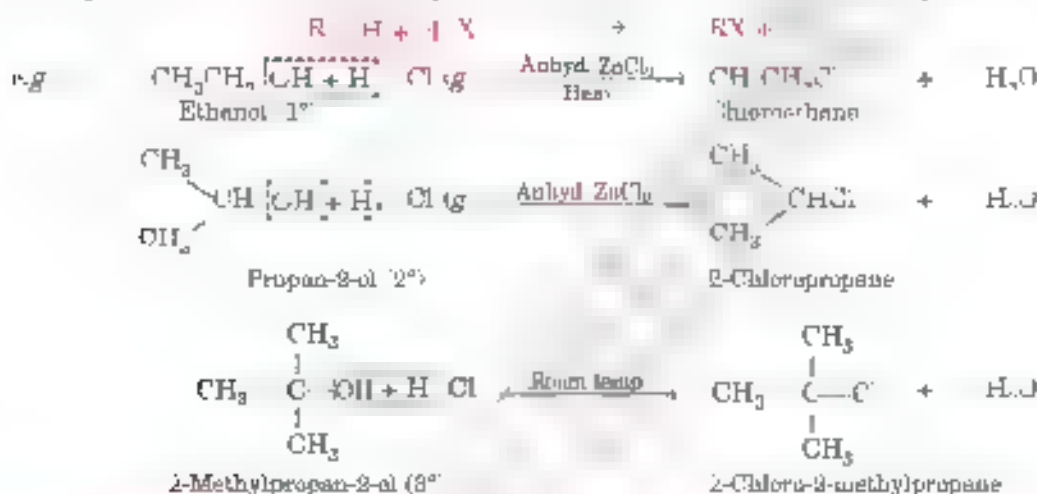


This is because I^- ion is a better nucleophile than Br^- ion, which in turn, is better than Cl^- ion.

The order of reactivity of alcohols is

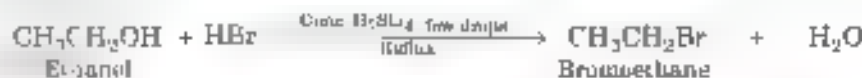


These trends have already been explained. Due to the low reactivity of primary and secondary alcohols with HCl, they require some Lewis acid catalyst for the reaction. In these reactions, anhydrous ZnCl_2 is used as a Lewis acid catalyst. However, no such catalyst is needed for the reaction of tertiary alcohols with HCl.



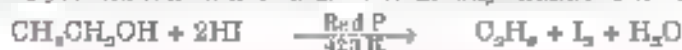
The reaction of primary and secondary alcohols with HCl gas in the presence of anhydrous ZnCl_2 is called **Groove's method**.

In the case of HBr, a small amount of conc. H_2SO_4 is also added as a catalyst for the reaction with primary alcohols. But no catalyst is added for the reaction with secondary and tertiary alcohols which get dehydrated in the presence of conc. H_2SO_4 .



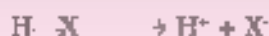
In the case of HI, alkyl iodides are formed by heating the alcohol with HI.

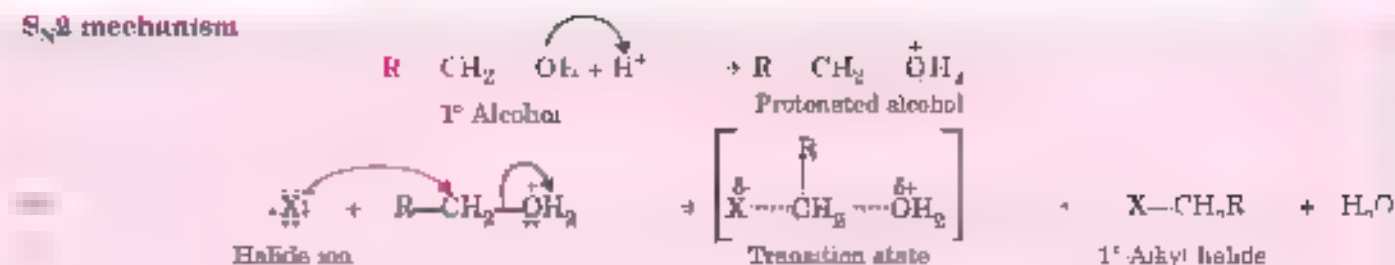
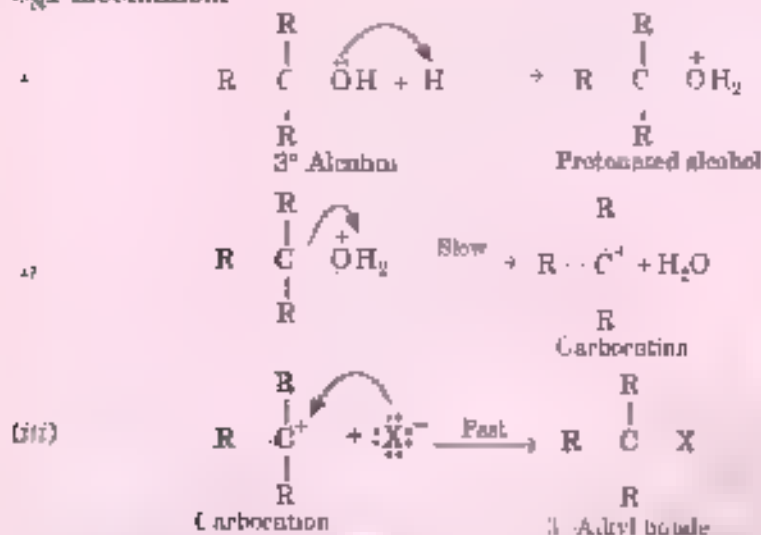
However, if reaction between hydrogen halide and alcohol is carried out in the presence of red phosphorus, alcohol gets reduced to hydrocarbon rather than to form alkyl halide. For example,



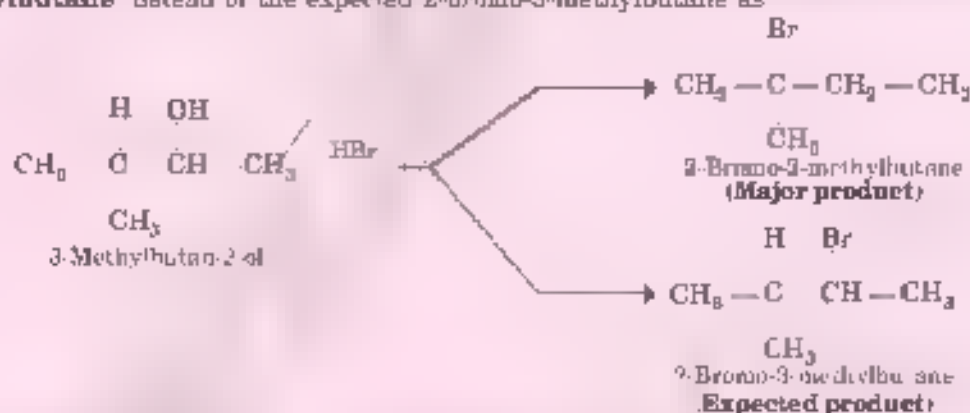
Mechanism: Reaction of alcohols with hydrogen halides.

The reactivity of the above reaction can be easily understood in terms of its **mechanism**. Primary alcohols react by $\text{S}_{\text{N}}2$ mechanism whereas secondary and tertiary alcohols react by $\text{S}_{\text{N}}1$ mechanism as

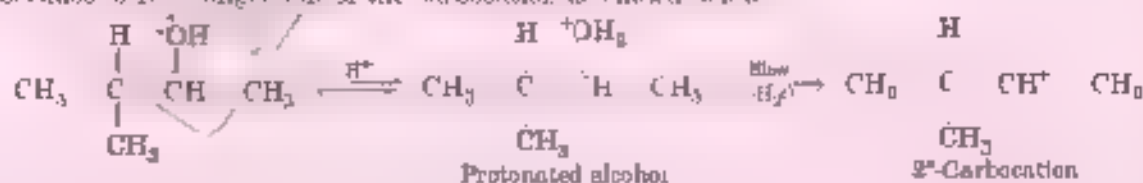


S_N2 mechanism**S_N1 mechanism**

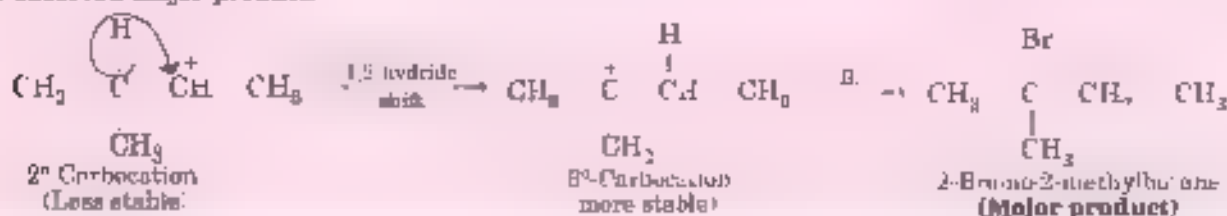
The reaction of 2° or 3° alcohols by S_N1 mechanism, after, gives rearranged products which are different from the expected products. As already learnt in Chapter 1, S_N1 reactions of alkyl halides, that is a 1,2-hydride or 1,2-methyl shift. For example, when 3-methylbutan-2-ol is treated with concentrated HBr the major product is **2-bromo-2-methylbutane** instead of the expected 2-bromo-3-methylbutane as



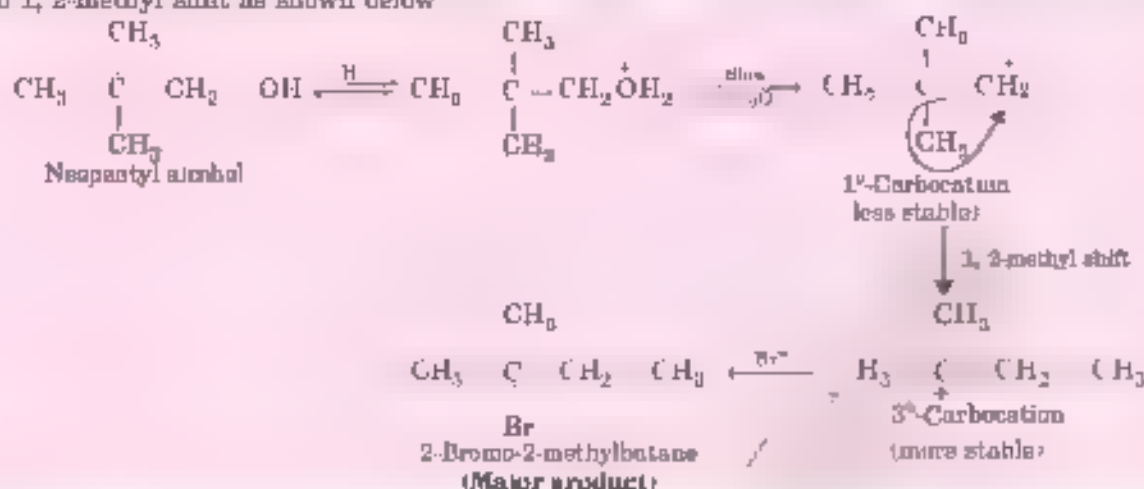
This is because of rearrangement of the carbocation, as shown below



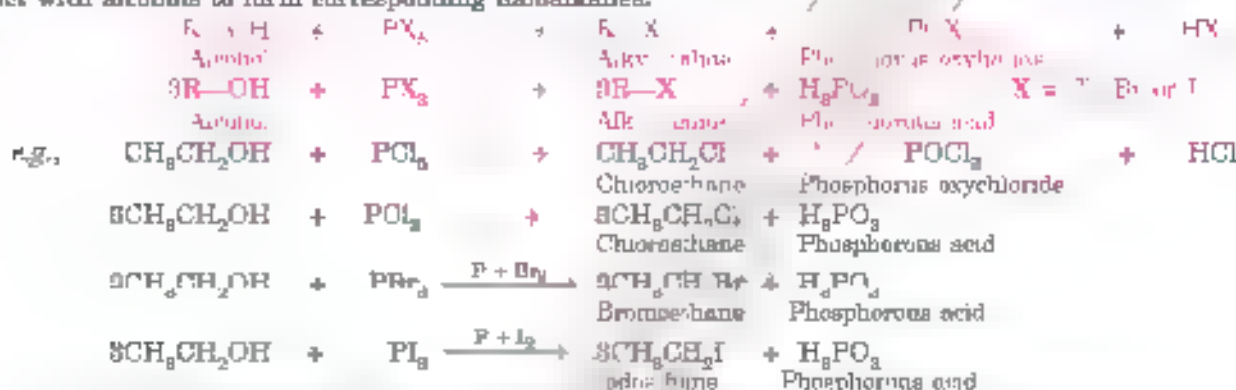
A hydride shift transforms the 2° carbocation into a more stable 3° carbocation and attack by bromide ion gives the observed major product.



Similarly neopentyl alcohol ($\text{CH}_3)_3\text{CCH}_2\text{OH}$ reacts with HBr to give **2-bromo-2-methylbutane** as rearranged product. This is due to 1, 2-methyl shift as shown below

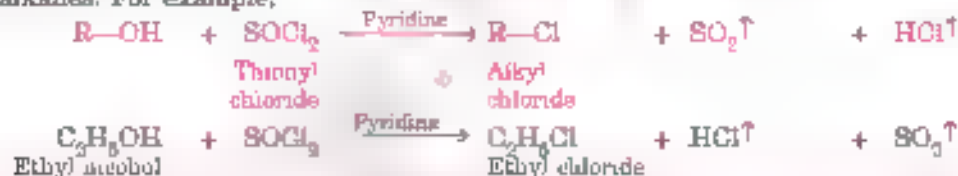


2. Reaction with phosphorus halides. Phosphorus halides such as PCl_5 , PCl_3 , PBr_3 , $\text{P} + \text{Br}_2$ or PI_3 , $\text{P} + \text{I}_2$, react with alcohols to form corresponding haloalkanes.



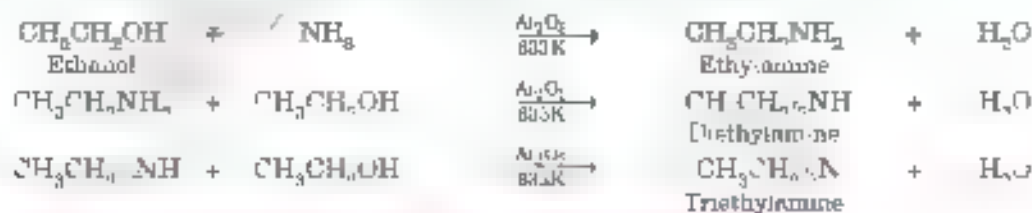
PBr_3 and PI_3 are generally prepared *in situ* by the reaction between phosphorus and bromine or iodine.

3. Reaction with thionyl chloride. On treatment with thionyl chloride in the presence of pyridine, alcohols form chloroalkanes. For example,



The reaction with thionyl chloride is preferred because the by products SO_2 and HCl formed are gases and can be easily removed from the reaction mixture.

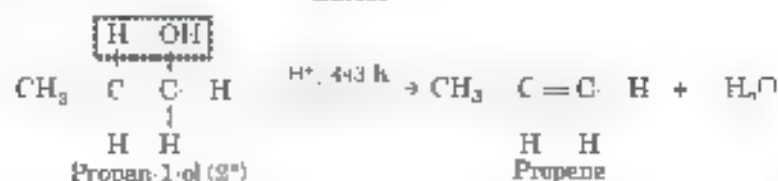
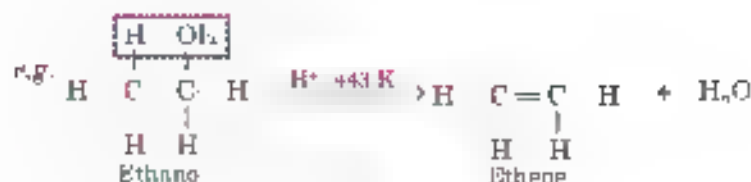
4. Reaction with ammonia. When vapours of an alcohol and ammonia are passed over heated calcium oxide at 633K, a mixture of primary, secondary and tertiary amines is produced. For example,



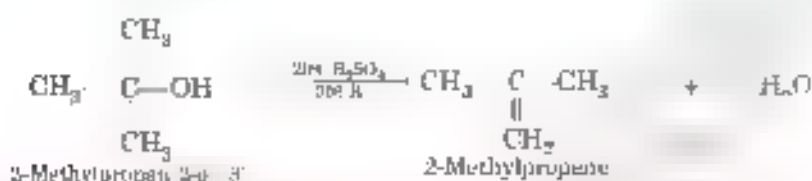
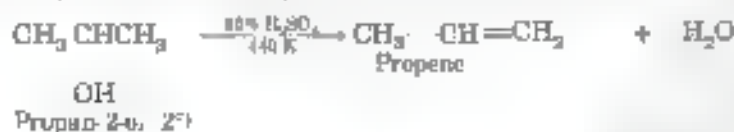
C. Reactions involving both the Cleavage of Alkyl and Hydroxyl Groups

1. Acidic dehydration. When alcohols are heated with a protic acid such as conc. H_2SO_4 or H_3PO_4 at 443 K, they get dehydrated to form alkenes.





Secondary and tertiary alcohols are dehydrated under mild conditions. For example,



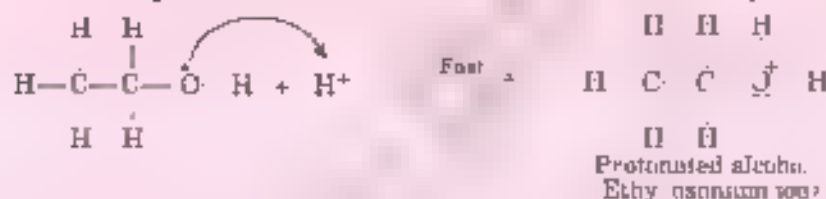
Thus, the relative ease of dehydration of alcohols follows the following order

Tertiary alcohol > Secondary alcohol > Primary alcohol

Reaction Mechanism : Acidic dehydration of alcohols

The reaction is believed to occur as follows

(i) **Formation of protonated alcohol.** Alcohol combines with a proton to form a protonated alcohol



(ii) **Formation of carbocation.** The protonated alcohol loses a water molecule to form a carbocation



(iii) **Elimination of a proton to form alkene.** The carbocation then eliminates a proton and undergoes rearrangement of electrons to form the alkene.



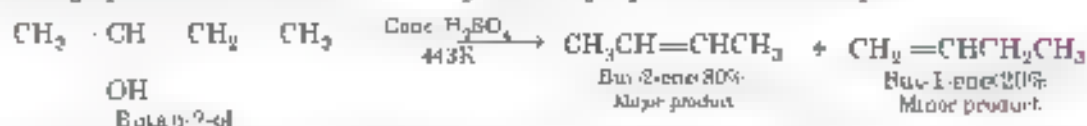
The acid used in step (i) is released in step (iii). To drive the equilibrium reaction in the forward direction, ethene is removed as soon as it is formed.

Some Important Facts about Dehydration of Alcohols Reaction

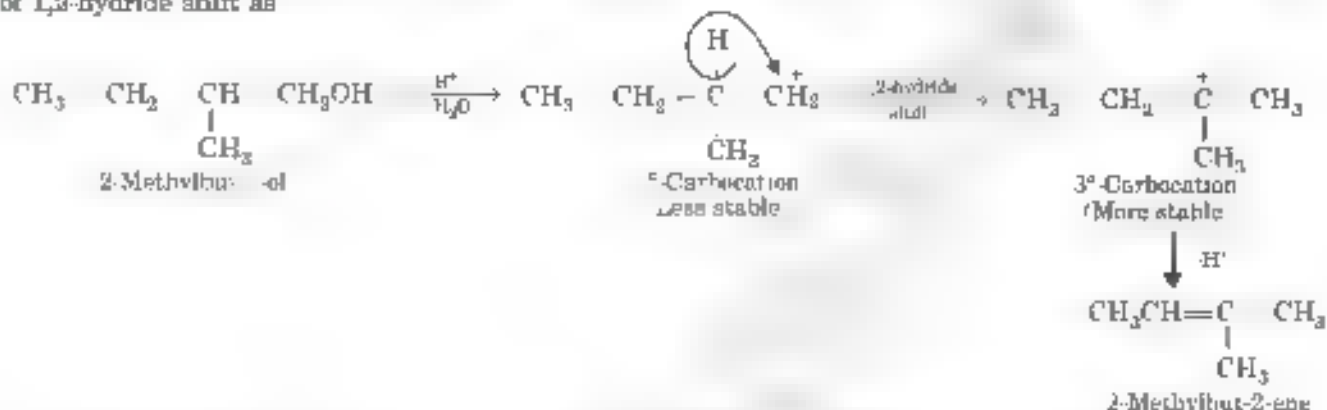
● The acidic dehydration of alcohols to alkenes occurs through the formation of an intermediate carbocation and the stability of carbocation follows the order $3^\circ > 2^\circ > 1^\circ$. Therefore, the relative ease of dehydration of alcohols follows the same order

Tertiary alcohol > Secondary alcohol > Primary alcohol

● The dehydration of 2° and 3° alcohols always occurs in accordance with **Saytzeff's rule**. According to this rule, the more highly substituted alkene is always the major product. For example,

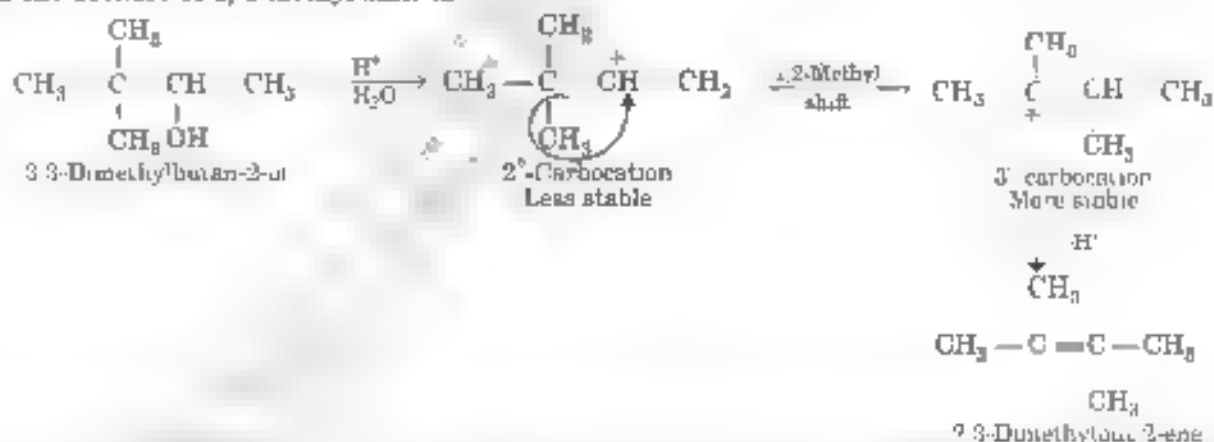


● Since the dehydration of alcohols involves the formation of intermediate carbocations which are always prone to rearrangements, therefore, the alkenes formed are always those obtained from rearranged carbocations. In the dehydration of 2-methylbutan-1-ol, the major product is 2-methylbut-2-ene instead of expected 2-methylbut-1-ene because of 1,2-hydride shift as



It may be noted that from 3°-carbocation the H^+ can be abstracted either from C-1 or from C-3. But it is preferably abstracted from C-3 to form more substituted alkene in accordance with Saytzeff's rule.

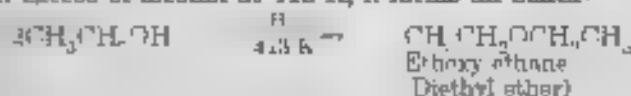
Similarly, 3,3-dimethylbutan-2-ol gives 2,3-dimethylbut-2-ene as the major product instead of expected 3,3-dimethylbut-1-ene because of 1,2-methyl shift as



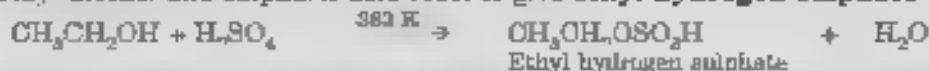
It may be noted that the reaction between alcohol and conc. H_2SO_4 depends upon the **conditions**. For example,

(i) At 443 K it gives **ethene** as the product.

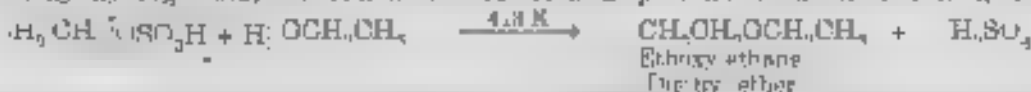
(ii) When heated with excess of alcohol at 413 K, it forms an **ether**.



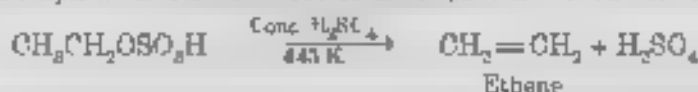
At 383 K, ethyl alcohol and sulphuric acid react to give **ethyl hydrogen sulphate**



When ethyl hydrogen sulphate is heated to 413 K in the presence of excess of alcohol, diethyl ether is formed.

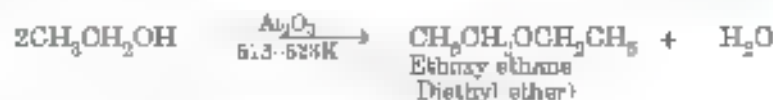


When ethyl hydrogen sulphate is heated to 443 K in the presence of excess of conc. H_2SO_4 , ethene is formed.



Dehydration of alcohols to ethers or a ketene can also be brought about by passing the vapour of the alcohols over **heated alumina catalyst** under different conditions

(a) At 513-523 K, ethers are obtained



b) At 833 K, alkenes are obtained



2 Oxidation The oxidation of alcohols involves the formation of a carbon-oxygen double bond with cleavage of an O—H and C—H bonds.

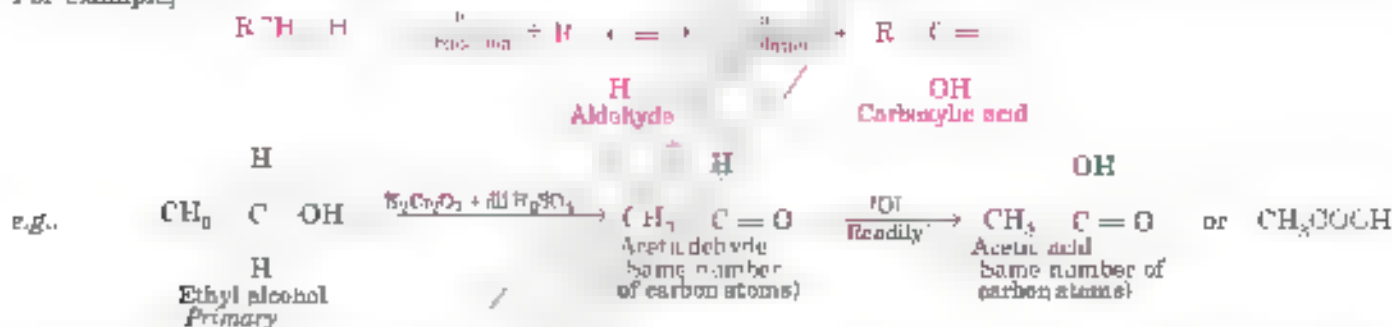


This type of cleavage and formation of bonds occur in oxidation reactions. These reactions are also called **dehydrogenation reactions** because these involve loss of hydrogen from an alcohol. The product of oxidation reaction depends upon the type of alcohol (primary, secondary or tertiary alcohol) as well as the nature of oxidising agent.

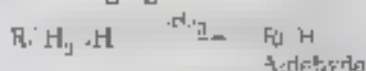
The oxidation of alcohols can be carried out by a number of reagents such as aqueous, alkaline or acidified KMnO_4 , acidified $\text{Na}_2\text{Cr}_2\text{O}_7$ or $\text{K}_2\text{Cr}_2\text{O}_7$, nitric acid, chromic acid etc. However, different classes of alcohols differ from each other not only in their ease of oxidation but also on the nature of products formed.

(i) **Primary alcohols.** A primary alcohol is easily oxidised to form first an aldehyde and then a carboxylic acid. Both the aldehyde and the acid formed contain the same number of carbon atoms as the starting alcohol.

For example,



Strong oxidising agents such as acidified potassium dichromate convert alcohols directly to carboxylic acids. However, oxidation can be stopped at aldehyde stage by using mild reagents in anhydrous medium such as CH_2Cl_2 as the oxidising agent.



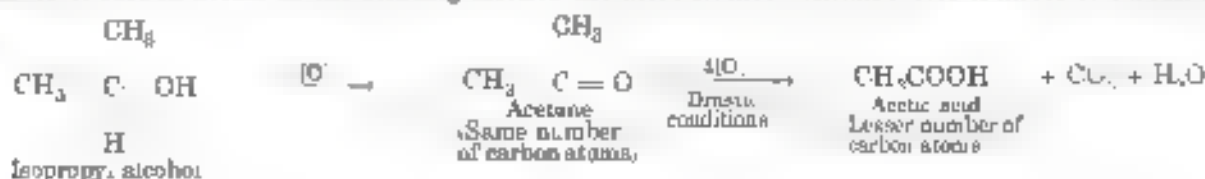
The common reagents used to stop oxidation of 1° alcohols to aldehyde stage are

- Collins reagent $\text{CrO}_2 \cdot 2\text{C}_5\text{H}_5\text{N}$, chromium trioxide pyridine complex
- PCC $\text{CrO}_2 \cdot \frac{1}{2}\text{C}_5\text{H}_5\text{N} \cdot \text{HCl}$ or $\text{C}_5\text{H}_5\text{NH} \cdot \text{CrCl}_2 \cdot \text{Cl}$, pyridinium chlorochromate
- PDC $(\text{C}_5\text{H}_5\text{NH})_2\text{Cr}_2\text{O}_7$, pyridinium dichromate

It may be noted that these reagents are very selective because these are useful for oxidation of alcohols which contain C—C double or triple bonds, allylic or benzylic C—H bonds.

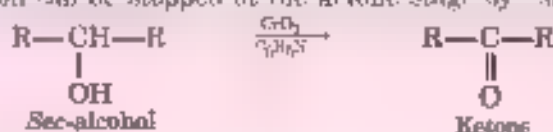


(ii) **Secondary alcohols.** A secondary alcohol is easily oxidised to form a ketone with chromic anhydride CrO_3 . The ketone may be further oxidised under strong conditions to form a mixture of acids. While the ketone contains the same number of carbon atoms as the starting alcohol, the acids formed contain lesser number of carbon atoms.

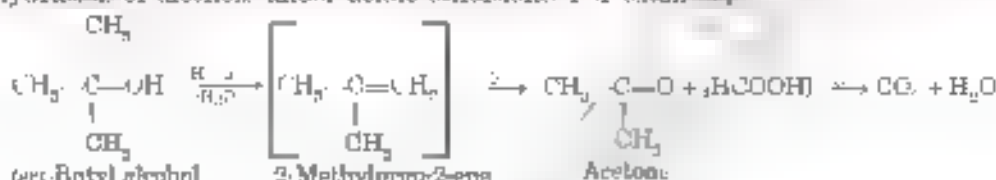




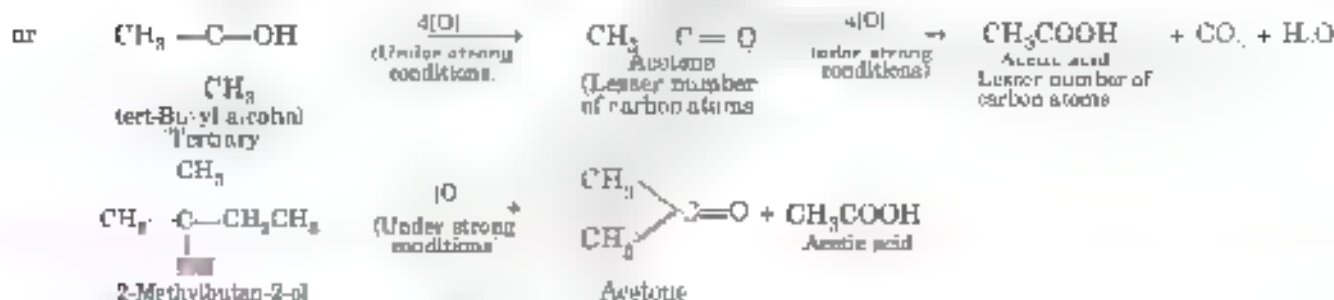
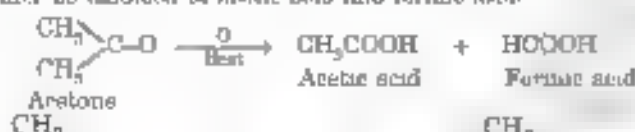
The oxidation can be stopped at the ketone stage by using chromic anhydride (CrO_3).



→ **Tertiary alcohols.** Tertiary alcohols are very difficult to be oxidised in neutral or alkaline KMnO_4 solution because they do not have hydrogen on carbon bearing $-\text{OH}$ group. However, when treated with acidic oxidising agents $\text{K}_2\text{Cr}_2\text{O}_7/\text{H}_2\text{SO}_4$ or $\text{KMnO}_4/\text{H}_2\text{SO}_4$ under very strong conditions at elevated temperature, cleavage of various $\text{C}-\text{C}$ bonds takes place. As a result, mixtures of ketones and carboxylic acids are formed. Both the ketones and acids contain lesser number of carbon atoms than the starting alcohols. The oxidation presumably occurs via alkene formation through dehydration of alcohols under acidic conditions. For example,



Acetone can further be oxidised to acetic acid and formic acid.

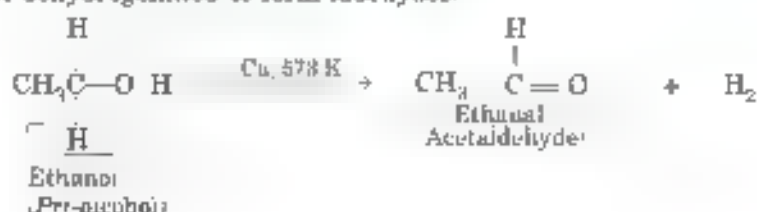


Be Curious →

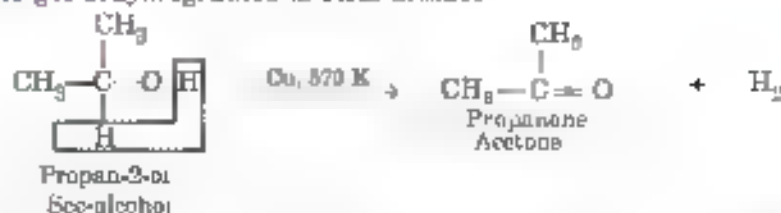
- ▶ Ethanol is generally used for drinking purposes. If a person consumes methanol by mistake, then how the person is treated for methanol poisoning?
- ▶ Biochemical oxidation of methanol or ethanol occurs in the body and produces the corresponding aldehyde and then the carboxylic acid. Methanol is oxidised first to methanal and then to methanoic acid while ethanol is oxidised first to ethanal and then to ethanoic acid. If an alcoholic person, by mistake, drinks denatured alcohol (i.e. ethanol mixed with methanol) the methanol is oxidised to methanoic acid which may cause blindness and even death. A methanol poisoned patient is treated by giving intravenous infusions of diluted ethanol (about 1% solution). Ethanol gets preferentially oxidised and slows down the oxidation of methanol. The enzyme causing the oxidation of ethanol ($-\text{CHO}$) to methanoic acid is swamped allowing time for kidneys to excrete methanol.

8. Dehydrogenation The dehydrogenation (removal of hydrogen) of alcohols is achieved when the vapours of alcohol are passed over copper heated at 573 K . Whereas the primary and secondary alcohols get easily dehydrogenated to form aldehydes and ketones respectively, tertiary alcohols get dehydrated (loses water molecule) under the reaction conditions to alkenes.

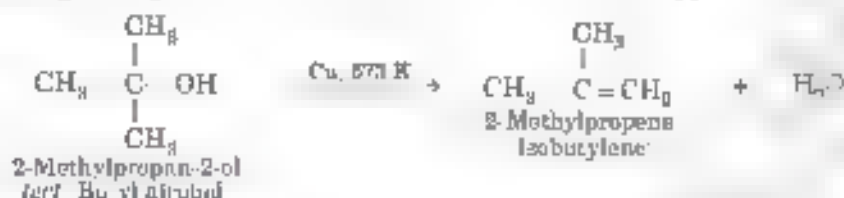
1) **Primary alcohols** get dehydrogenated to form aldehydes.



(ii) Secondary alcohols get dehydrogenated to form ketones.



(iii) Tertiary alcohols get dehydrated on treatment with hot reduced copper to form alkenes.



CHEMICAL PROPERTIES OF PHENOLS

The phenols are reactive compounds. The chemical properties of phenols are of three types

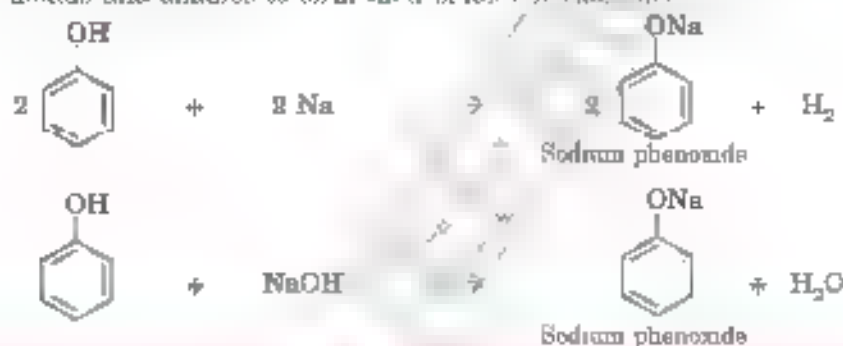
A. Reactions of phenolic group (—OH group).

B. Reactions of benzene ring

C. Special reactions

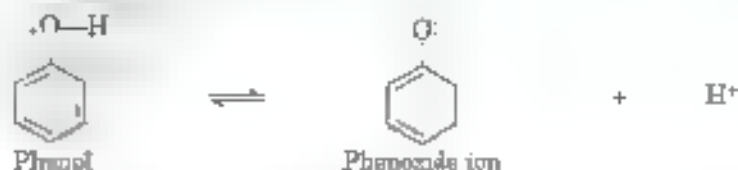
A. Reactions of Phenolic (—OH) Group

1. **Acidic character.** Phenols are weakly acidic in nature ($K_a = 10^{-8}$ to 10^{-10}). They turn blue litmus red and react with alkali metals and alkalis to form their salts. For example,

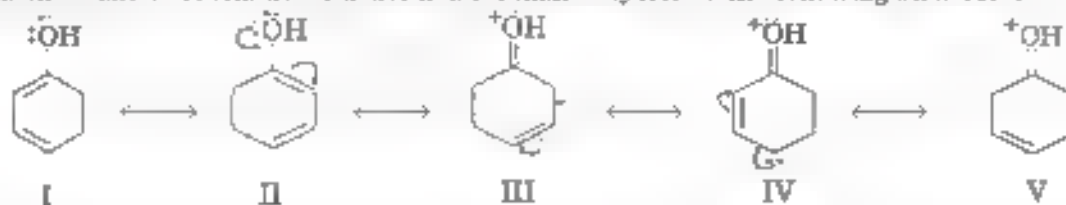


However phenol is weaker acid than carboxylic acid. Therefore like carboxylic acids, phenol does not react with Na_2CO_3 and sodium bicarbonate (NaHCO_3 , evolving CO_2).

The acidic character of phenol is because of the presence of polar O—H group. The hydroxyl group in phenol is directly attached to the sp^2 hybridised carbon of benzene ring which acts as an electron withdrawing group. Due to the higher electronegativity of sp^2 hybridised carbon of phenol to which —OH is attached, electron density on oxygen increases. This increases the polarity of O—H bond and results in an increase in ionisation of phenols. As a result H^+ ion can be easily released from aqueous solution as

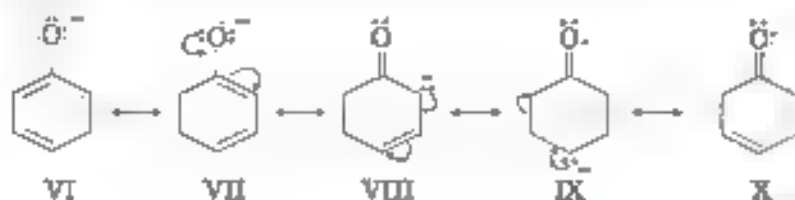


Phenols are more acidic than alcohols. The greater acidic character of phenols as compared to alcohols can be explained on the basis of resonance. Phenol is a resonance hybrid of the following structures



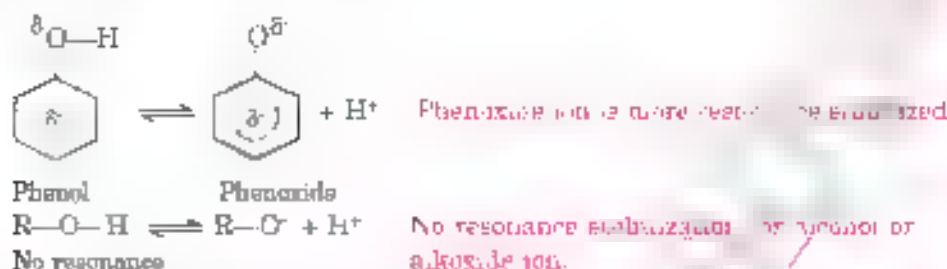
It is clear that three structures of phenol (III, IV and V) have +ve charge on oxygen of —OH group. This oxygen

attracts the electron pair of O-H bond strongly towards itself weakens the O-H bond and, therefore, facilitates the release of H^+ . Similarly the phenoxide ion is resonance stabilized as follows



Thus, we observe that both phenol and phenoxide ion are stabilized by resonance. Now if we carefully observe the resonance structures, we observe that phenoxide ion is more resonance stable than phenol. In phenol three contributing structures III, IV and V have both positive and negative charges and therefore, these will be unstable. These structures will require energy to separate the charge and therefore, will be unstable. On the other hand, there is no structure in phenoxide ion which requires charge separation. Thus, the resonance hybrid of phenol is less stable than phenoxide ion and the reaction is very much in favour of the phenoxide ion. Therefore, the phenol is more acidic.

On the other hand, in case of alcohols, neither the alcohol nor the alkoxide ion is stabilized by resonance



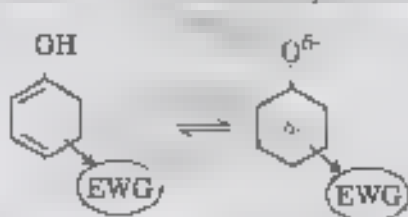
Thus, phenols are more acidic than alcohols. However, phenols are less acidic than carboxylic acids which is supported by their dissociation constant K_a values

Compound	Ethanol	Phenol	Ethanoic acid
K_a	10^{-16}	10^{-10}	10^{-5}

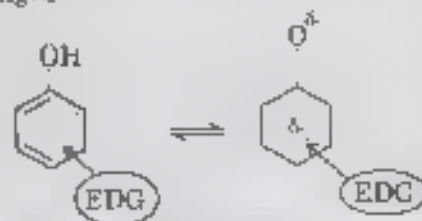
Effect of Substituents on the Acidic Character of Phenols

The effect of substituents on the acidic character of phenols can be easily understood in terms of stability of phenoxide ion relative to phenol. Any group that stabilizes the phenoxide ion more than the acid would make the reaction more towards forward direction and would increase the acidity. In the other hand, a group that makes the phenoxide ion less stable would decrease the acidity.

a. Electron withdrawing substituents (EWG) like NO_2 , CN , X (halogen), etc. withdraw electrons and disperse the negative charge on phenoxide ion. Therefore, these substituents stabilize the phenoxide ion relative to phenol. Thus, these groups will increase the acidic strength.



Electron withdrawing group withdraws electrons, disperses the negative charge and therefore stabilizes the phenoxide ion w.r.t phenol.
Acidic strength increases.



Electron donating group donates electrons, intensifies the -ve charge and therefore destabilizes the phenoxide ion w.r.t phenol.
Acidic strength decreases.

b. Electron donating groups (EDG) like R (alkyl), NH_2 , OR (alkoxy), etc. give electrons and intensify the negative charge on phenoxide ion. Therefore, these substituents destabilize the phenoxide ion relative to phenol. Thus, these groups will decrease the acidic character.

HELP

The acidic character of an acid is expressed in terms of K_a (dissociation constant).

The stronger the acid, the larger will be its K_a value.

Alternately, K_a may also be expressed as pK_a , which is defined as $pK_a = \log K_a$.

Smaller the pK_a value, stronger is the acid.

The acidity constant (pK_a) of some phenols are given below

Electron withdrawing groups		Electron releasing groups	
Phenol	pK_a	Phenol	pK_a
<i>p</i> -Chlorophenol	9.38	<i>p</i> -Aminophenol	10.46
<i>p</i> -Bromophenol	9.35	<i>p</i> -Methoxyphenol	10.21
<i>p</i> -Nitrophenol	7.15	<i>p</i> -Methylphenol	10.17
2, 4, 6-Trinitrophenol	0.60		
Phenol		9.98	

The partitioning effect is more significant when the substituent is present at *o*- or *p*-position than *m*-position to the $-CH_3$ group. This means that *o*- and *p*-cresols will be more acidic than *m*-cresol and *p*-methylphenols (cresols) will be less acidic than *m*-cresol.

Thus, acidic strength decreases as



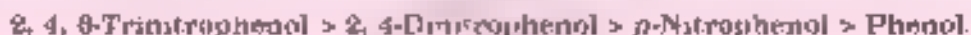
Similarly,



Alcohol	pK_a	Alcohol	pK_a
<i>o</i> -Nitrophenol	7.22	<i>o</i> -Cresol	10.28
<i>o</i> -Nitrophenol	8.90	<i>m</i> -Cresol	10.08
<i>p</i> -Nitrophenol	7.15	<i>p</i> -Cresol	10.14

Presence of more than one substituents also increases or decreases the acidic strength.

For example,

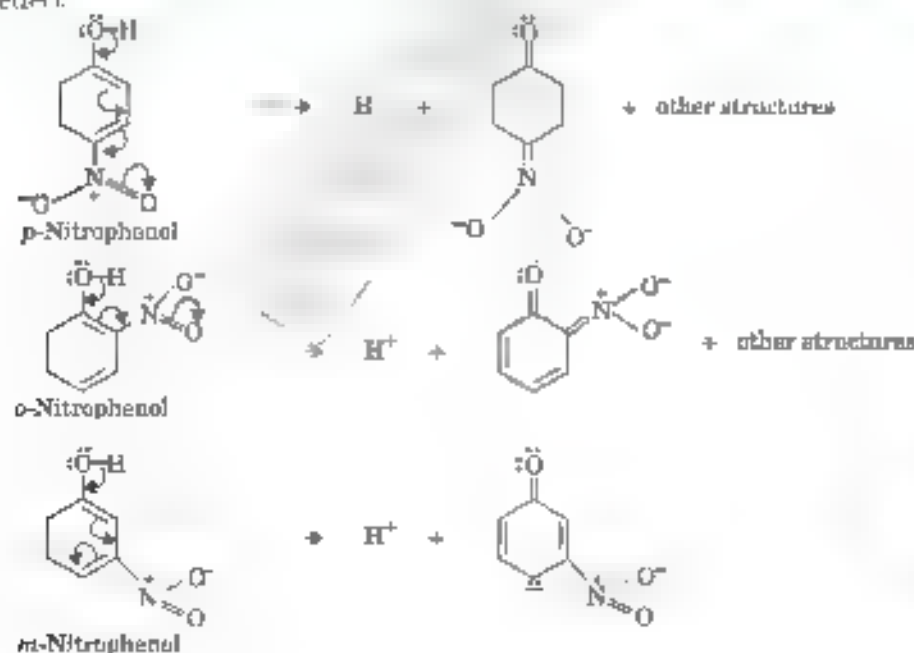


pK_a	0.71	4.0	7.15	9.98
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COMPARISON OF ACIDIC STRENGTH OF PHENOLS

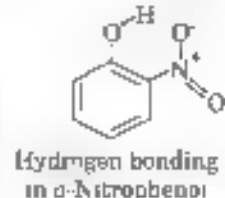
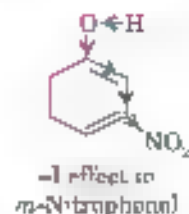
(a) Comparison of acidic strength of nitrophenols

The nitro group ($-NO_2$) has both $-R$ effect and $-I$ effect. But the $-R$ effect predominates over the $-I$ effect. Due to strong electron withdrawing nature of $-NO_2$ group, all the nitrophenols are more acidic than phenol. When $-NO_2$ group is present at *o*- and *p*-positions, it withdraws electrons of the $O-H$ bond towards it by stronger $-R$ effect whereas when $-NO_2$ group is present at *m*-position, it withdraws electrons of $O-H$ bond only by weaker $-I$ effect.



When $-NO_2$ is at *o*- and *p*-position the conjugation is extended up to oxygen atom of the nitro group and the anion is more stable than *m*-nitrophenoxide where no such conjugation is possible.

It is clear from the above structures that when NO_2 group is at *o*- and *p*-positions, nitrophenoxide ion is more resonance stable because the conjugation is extended upto oxygen atom of the nitro group. But the *m*-nitrophenoxide ion is less stable because no such conjugation is possible in its structures. Thus, *o*- and *p*-nitrophenols are more acidic than *m*-nitrophenol. The larger acidic character of *o*-nitrophenol is only because of $-I$ effect as shown.



However, *o*-nitrophenol is slightly weaker acid than *p*-nitrophenol because of intramolecular hydrogen bonding which makes loss of a proton little difficult.

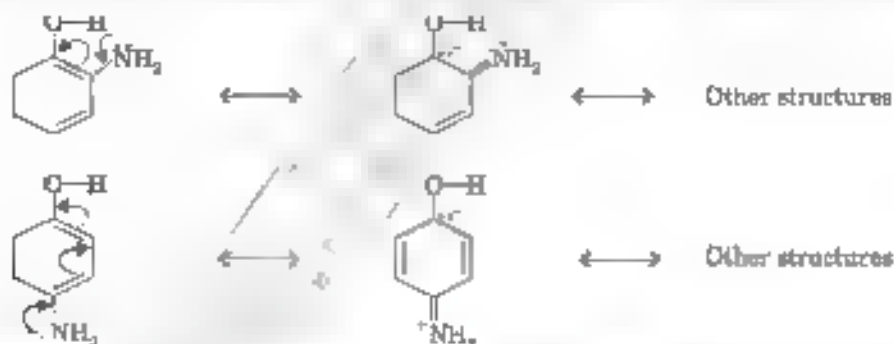
(b) Comparison of acidic strength of cresols (methylphenols)

Methyl group $-\text{CH}_3$ has $+I$ effect and hyperconjugation effect. But the hyperconjugation effect predominates over $+I$ effect. Both these effects, increase the electron density in the $\text{O}-\text{H}$ bond so that the loss of proton becomes little difficult. Hence, **all the cresols are weaker acids than phenol**. Since hyperconjugation effect can operate only at *o*- and *p*-positions and not through *m*-position, therefore, *o*- and *p*-cresols are less acidic than *m*-cresol. However, as we know that $+I$ effect of a substituent decreases with the increase in distance from the reaction centre, therefore, $+I$ effect will be more at *o*-position than at *p*-position. Due to stronger $+I$ effect at *o*-position than at *p*-position, *o*-cresol is a weaker acid than *p*-cresol. Thus, acidic strength decreases as

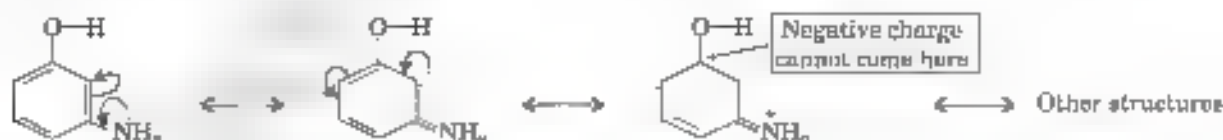


(c) Acidic strength of aminophenols and methoxyphenols

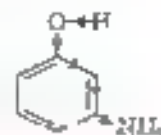
An amino group $-\text{NH}_2$ and a methoxy group $-\text{OCH}_3$ when attached to the benzene ring have $+R$ effect due to the presence of lone pair of electrons on N or O atom as well as $-I$ effect due to electron withdrawing nature of these groups. N and O are more electronegative than C. When $-\text{NH}_2$ group (or $-\text{OCH}_3$ group) is present at *o*- or *p*-position w.r.t $-\text{OH}$ group, it increases electron density in the $\text{O}-\text{H}$ bond by $+R$ effect of $-\text{NH}_2$ group (or $-\text{OCH}_3$ group).



However, when $-\text{NH}_2$ group (or $-\text{OCH}_3$ group) is present at *m*-position, it cannot push electrons into the $\text{O}-\text{H}$ bond because negative charge cannot move to the carbon atom to which $-\text{H}$ bond is attached.

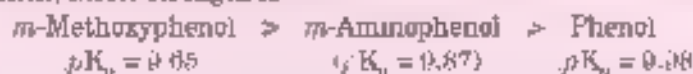


Since $-\text{NH}_2$ group cannot exert $+R$ effect at *m*-position, therefore it exerts only $-I$ effect. Therefore, it withdraws electrons from all the nuclear positions of the benzene ring and hence withdraws electrons of $\text{O}-\text{H}$ bond. As a result, the electron density in $\text{O}-\text{H}$ bond decreases and hence *m*-aminophenol is more acidic than *o*- and *p*-aminophenols.



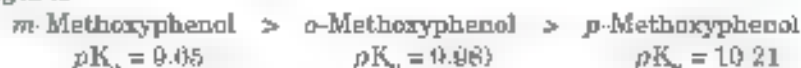
Similarly, *m*-methoxyphenol is more acidic than *o*- and *p*-methoxyphenols due to $-I$ effect of $-\text{OCH}_3$ group.

Now $-I$ effect of methoxy group $-\text{OCH}_3$ is more than that of $-\text{NH}_2$ group, therefore, *m*-methoxyphenol is more acidic than *m*-amino phenol. Thus, acidic strength is



On comparing *o*- and *p*-methoxyphenols, +R effect on *o*-position is less than at *p*-position because of steric hindrance. As a result, the increase in electron density in O-H bond is less in case of *o*-methoxyphenol than *p*-methoxyphenol. Consequently, *o*-methoxyphenol is slightly more acidic than corresponding *p*-isomer.

Thus, the acidic strength is

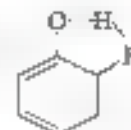
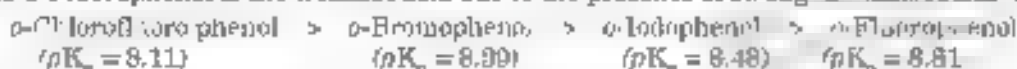


(d) Comparison of acidic strength of halophenols

Halogens have both +R effect and -I effect but -I effect predominates over the +R effect. Therefore, all **halophenols (except *p*-fluorophenol) are more acidic than phenol**. As we know, -I effect decreases with distance, therefore, acidic strength of halophenols is



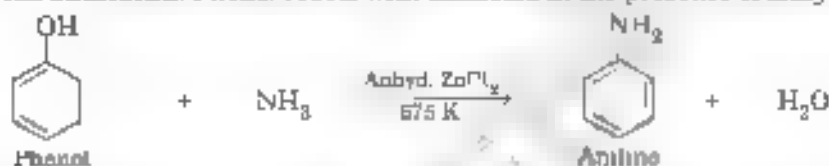
Amongst *o*-halophenols, the acidic strength of *o*-phenols decreases as -I effect of the halogen decreases except for *o*-fluorophenol. *o*-Fluorophenol is the weakest acid due to the presence of strong intramolecular hydrogen bonding.



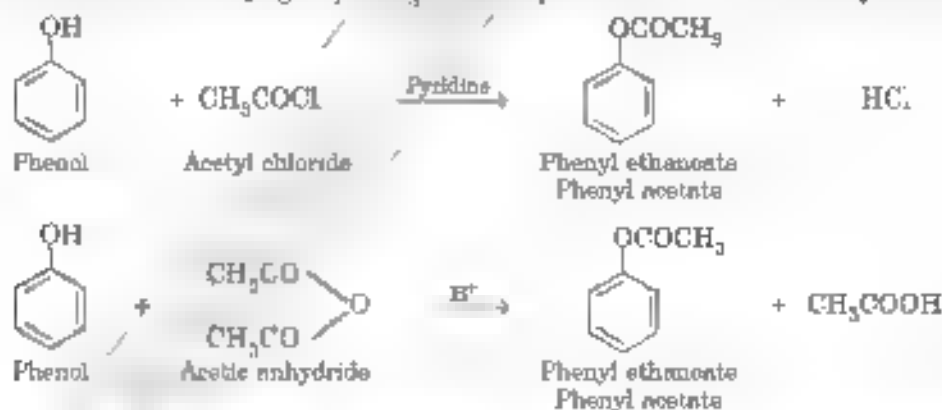
2. Action with zinc dust. When heated with zinc dust, phenol is reduced to benzene.



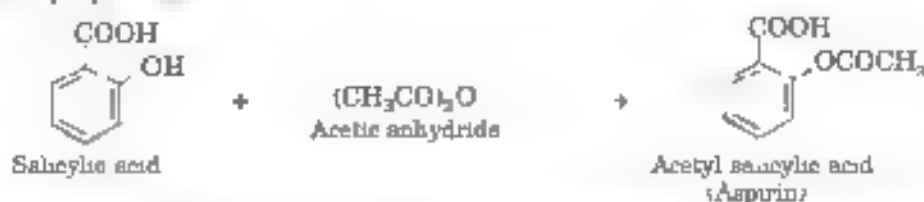
3. Action with ammonia. Phenol reacts with ammonia in the presence of anhydrous zinc chloride to give aniline.



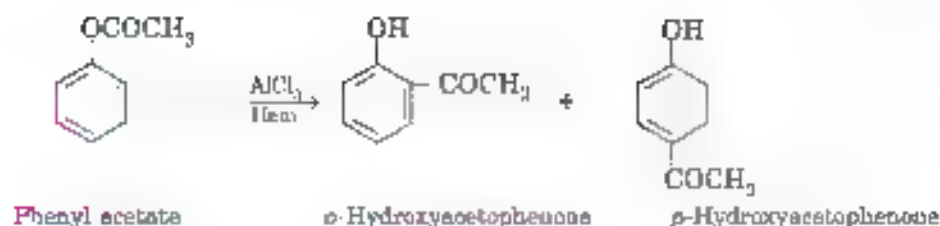
4. Action with acid chlorides and acid anhydrides (acylation). When treated with acetyl chloride in the presence of pyridine or acetic anhydride in the presence of small amount of conc. H_2SO_4 , esters are formed. This reaction is reversible in nature. The pyridine base removes HCl formed. It also shifts the equilibrium to the right-hand side. The introduction of acetyl group (CH_3CO) in phenol is known as **acetylation reaction**.



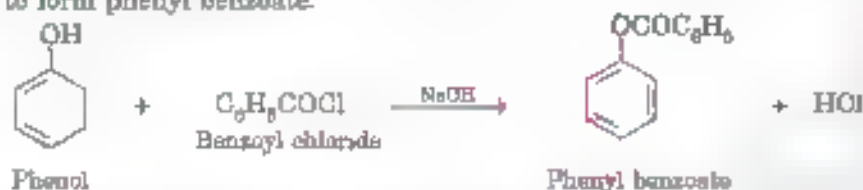
Acetylation of salicylic acid produces **aspirin** (acetyl salicylic acid) which has analgesic, anti-inflammatory, and anti-pyretic properties.



When phenyl acetate is heated with anhydrous $AlCl_3$, it undergoes rearrangement in which acyl group migrates from the phenolic oxygen to an ortho and para positions forming ortho and para hydroxy ketones. This reaction is called **Fries rearrangement**.



5. Action with benzoyl chloride (benzoylation). Phenols react with benzoyl chloride in the presence of aqueous NaOH to form phenyl benzoate.



This reaction is called **Schotten Baumann reaction**.

6. Reaction with Grignard reagent. Like alcohols phenols also react with Grignard reagent to form alkanes.

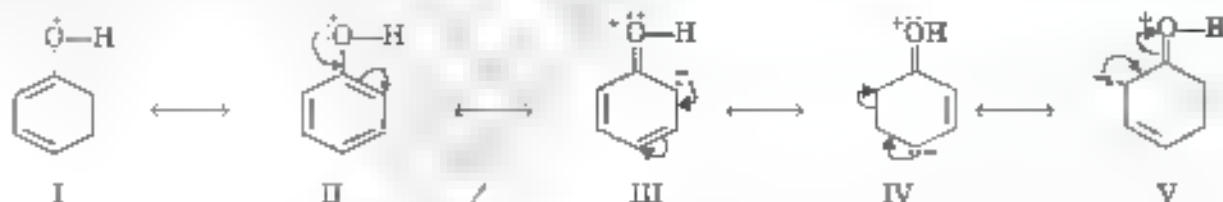


NOTE

As in case of alcohols the alkane formed corresponds to the alkyl group of the Grignard reagent.

B. Reactions of Benzene Ring Electrophilic Substitution Reactions

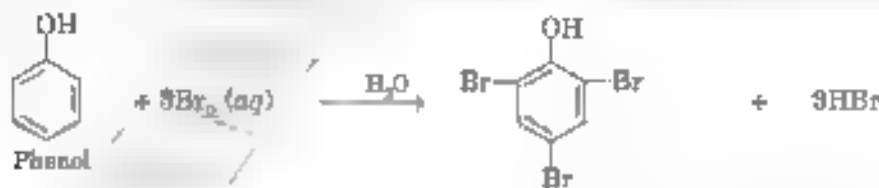
Apart from reactions that directly affect the -OH group, phenol undergoes *electrophilic aromatic substitution reactions*. As the -OH group is an *activating group*, these reactions occur at a **faster rate** than reactions of benzene itself. The -OH group is **ortho-para directing** and therefore, incoming group comes at ortho or para position. This is due to the reason that because of electronic effects caused by -OH group, the ortho and para positions become electron rich as shown below.



o- and p-positions are electron rich sites

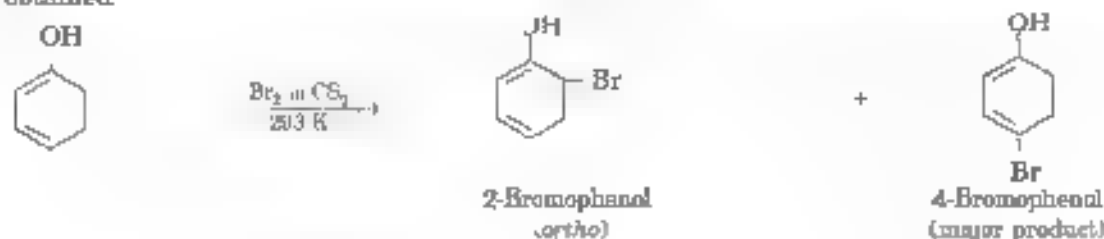
Some common examples are

1. Bromination. Phenol reacts with bromine water (aqueous solution) to give a precipitate of 2, 4, 6-tribromophenol.



2, 4, 6-Tribromophenol
(White ppt.)

However, if the reaction is carried out in CS_2 or CCl_4 at a low temperature, a mixture of *ortho* and *para* bromophenol is obtained.

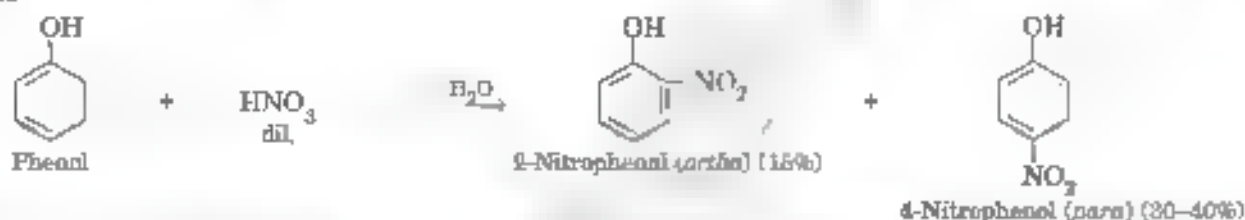


It may be noted that the usual halogenation is carried out in the presence of Lewis acid, Fe-Br_3 which polarises the halogen molecule. In case of phenol, the polarisation of bromine occurs even in the absence of Lewis acid. This is because of highly activating effect of $-\text{OH}$ group on the benzene ring. The reaction is believed to occur as

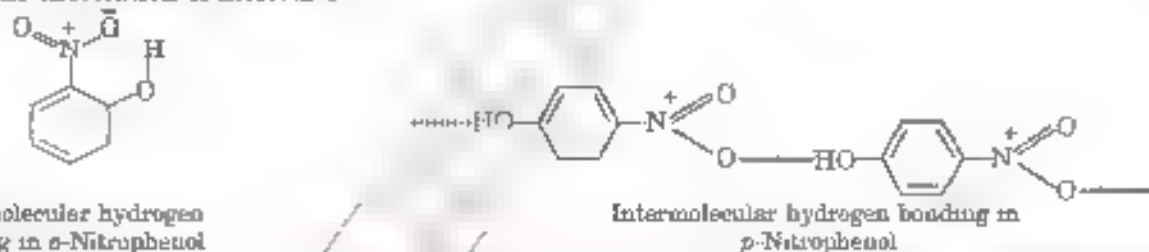


Explanation. In aqueous solution, phenol ionizes to give phenoxide ion. Due to the presence of the negative charge, the oxygen atom of the phenoxide ion donates electrons to the benzene ring to a large extent. As a result, the ring gets highly activated leading to the formation of trisubstituted product. On the other hand, in the non-polar solvents, the ionization of phenol does not occur to a large extent. As a result, the $-\text{OH}$ group donates electrons to the benzene ring only to a small extent. Consequently, the ring is activated slightly and, therefore, only monosubstitution occurs.

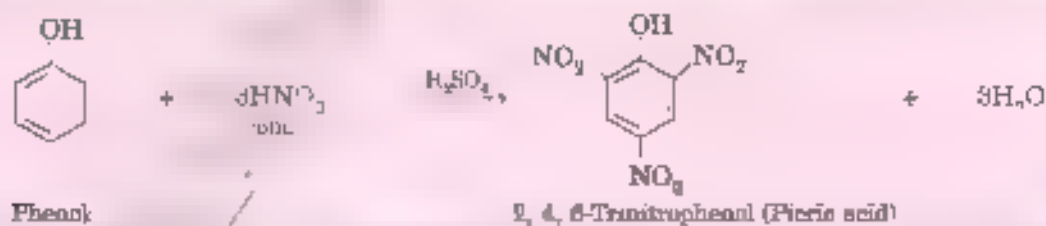
2. Nitration. Phenol reacts with dilute nitric acid at low temperature (298 K) to give a mixture of ortho and para nitrophenol.



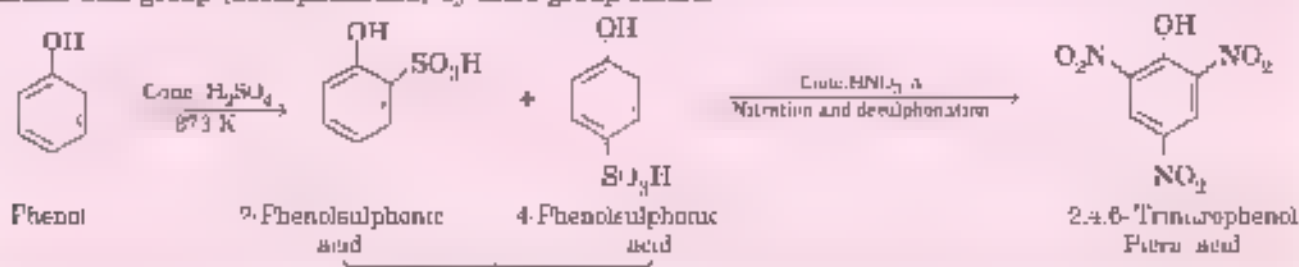
The ortho and para isomers can be separated by steam distillation. *o*-Nitrophenol is steam volatile due to intramolecular hydrogen bonding while *p*-nitrophenol is less volatile because of intermolecular hydrogen bonding which causes the association of molecules.



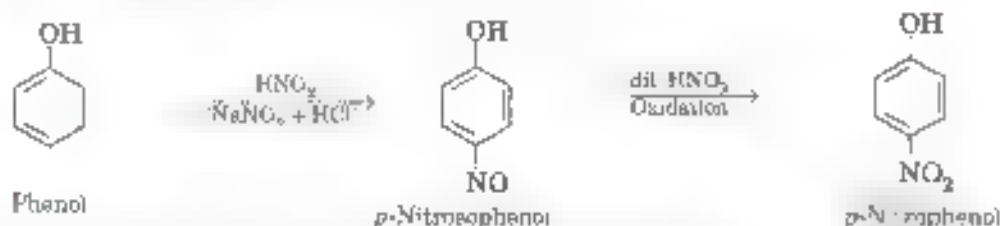
With conc. nitric acid, in the presence of sulphuric acid, phenol gives 2, 4, 6-trinitrophenol (picric acid). The yield of nitro product is low because of the oxidation of ring by conc. HNO_3 .



Now a days picric acid is prepared by treating phenol first with conc. H_2SO_4 at 373 K when a mixture of 2-phenolsulphonic acid and 4-phenolsulphonic acid is formed. This mixture is then heated with conc. HNO_3 to form 2,4,6-trinitrophenol (picric acid) in about 80% yield. During this reaction, nitration with simultaneous replacement of the sulphonic acid group (desulphonation) by nitro group occurs.

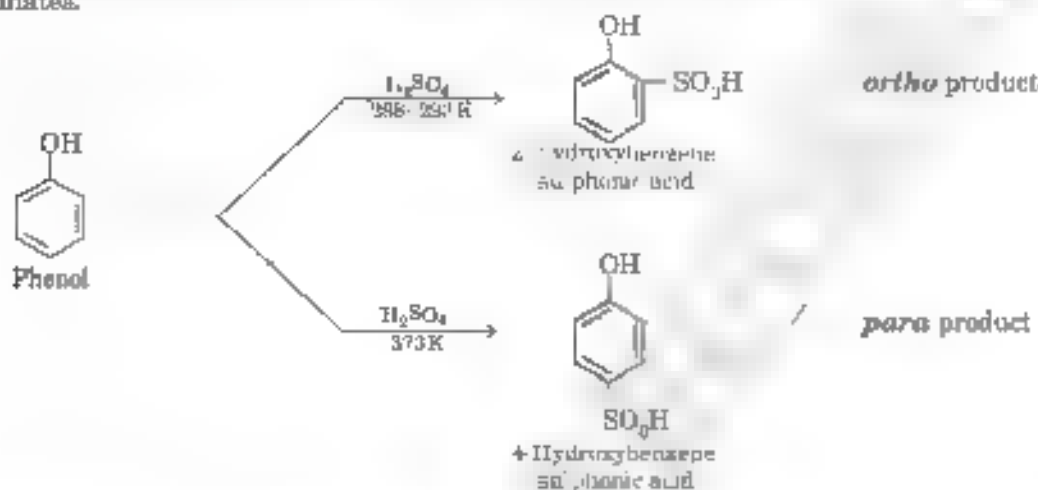


3. Nitrosation: Phenol reacts with nitrous acid $\text{NaNO}_2 + \text{HCl}$ at low temperature 283 K to form *p*-nitrosophenol. The reaction in which an *ortho* to the substitution by a *nitro* group $-\text{NO}$ is called **nitrosation**. The *p*-nitrosophenol can be further oxidised with dil. HNO_3 to give *p*-nitrophenol.



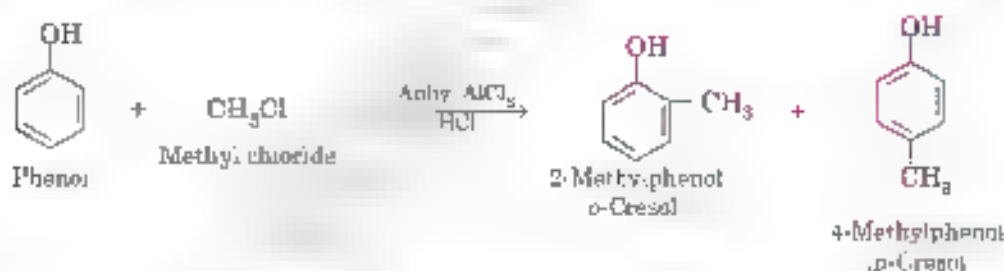
Therefore, the above method is used to get better yield of nitrophenols.

4. Sulphonation: Phenol reacts with conc. sulphuric acid to form a mixture of *ortho* and *para*-phenol sulphonic acid. At low temperature 288 K *ortho* isomer is the main product while at higher temperature 373 K the *para* isomer predominates.



When 2-hydroxybenzene sulphonic acid is heated to 373 K , it gives thermodynamically controlled 4-hydroxybenzene sulphonic acid.

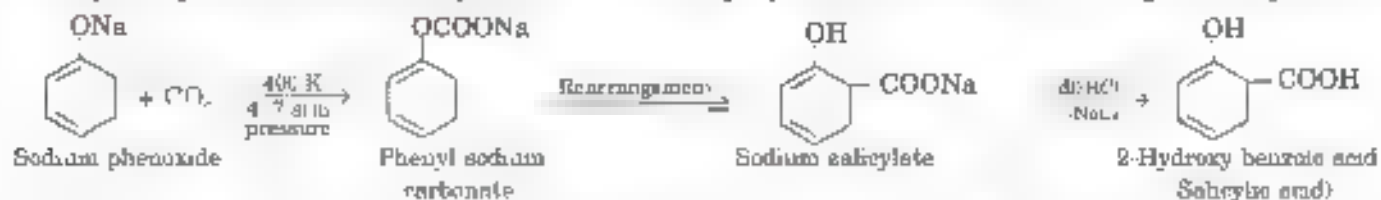
5. Friedel Crafts Alkylation: When phenol is treated with alkyl halides in the presence of anhydrous aluminium chloride, it forms cresols. The reaction is called **Friedel Crafts alkylation reaction**.



The yield of alkyl phenols is generally low because AlCl_3 coordinates with the oxygen atom.

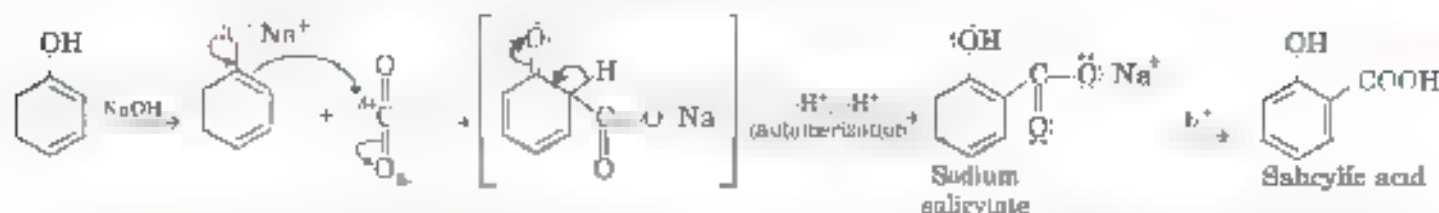
C. Special Reactions of Phenol

1. Kolbe's reaction: When sodium phenoxide is treated with carbon dioxide at about 400 K and under 4 to 7 atmospheric pressure sodium salicylate is formed as major product. This on acidification gives salicylic acid.



A small amount of *para* isomer is also obtained and if the temperature be allowed to rise above 400 K , the *para* isomer dominates. The reaction is called **Kolbe's reaction**. In the Kolbe's reaction, carbon dioxide acts as the

electrophile The mechanism involves the attack of CO_2 on highly activated phenoxide ion.

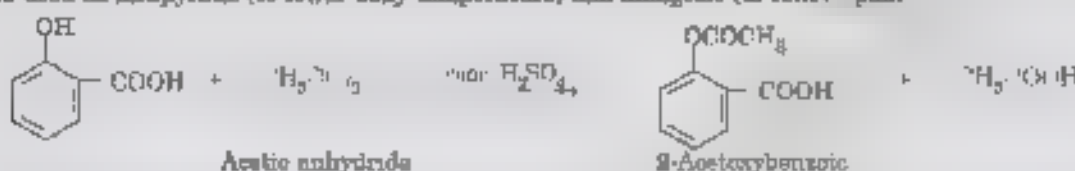


The reaction is usually carried out by allowing sodium phenoxide to absorb carbon dioxide and then heating the product to 400 K and 4–7 atm pressure. First unstable intermediate is formed which undergoes a proton shift to form sodium salicylate. The subsequent acidification of sodium salicylate gives salicylic acid.

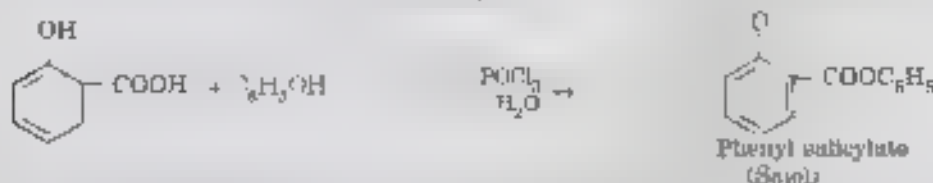
Salicylic acid is the starting material for the manufacture of a number of **important compounds**.

For example:

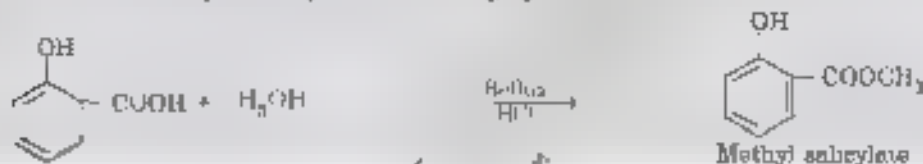
(i) **Aspirin (2-acetoxy benzoic acid)** – It is obtained by acetylating salicylic acid with acetic anhydride and conc. H_2SO_4 . Aspirin is used as antipyretic (to lower body temperature), and analgesic (to relieve pain).



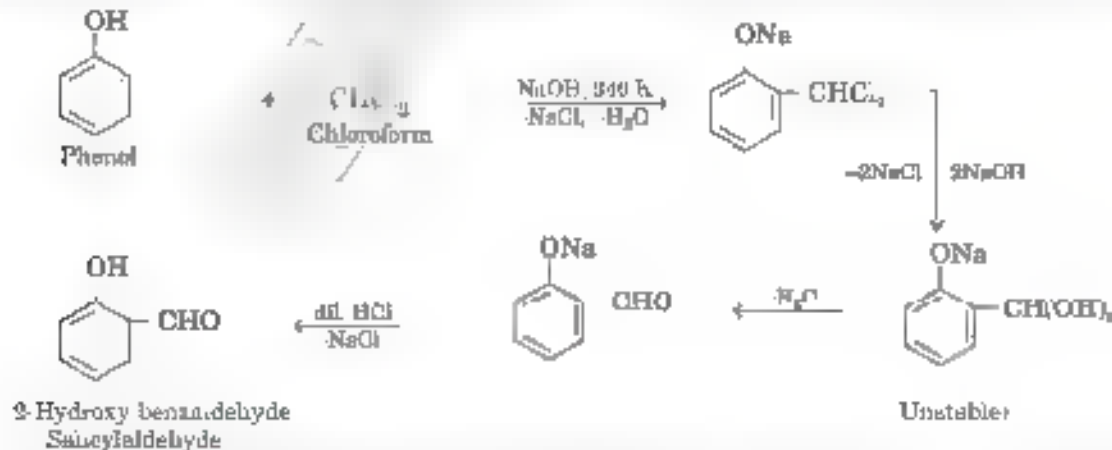
(ii) **Salo (phenyl salicylate)**: It may be prepared by heating salicylic acid with phenol in the presence of phosphoryl chloride. Salol is used as an intestinal antiseptic.



(iii) **Methyl salicylate** (constituent of oil of winter green) is prepared by refluxing salicylic acid with methyl alcohol. It is used in perfumery as a flavouring agent.



2. Reimer-Tiemann reaction: When phenol is refluxed with chloroform in the presence of aqueous sodium hydroxide at 340 K followed by hydrolysis, an aldehydic group $-\text{CHO}$ gets introduced in the ring at a position ortho to the phenolic group. *Ortho*-hydroxy benzaldehyde or salicylaldehyde is formed as the product of the reaction.



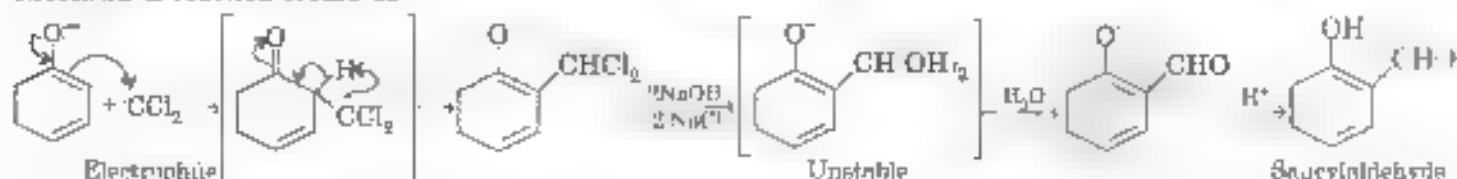
This reaction is called **Reimer-Tiemann reaction**. In addition to *o*-salicylaldehyde, small amount of *p*-salicylaldehyde is also formed but the major product is *ortho*.

Reimer-Tiemann reaction :

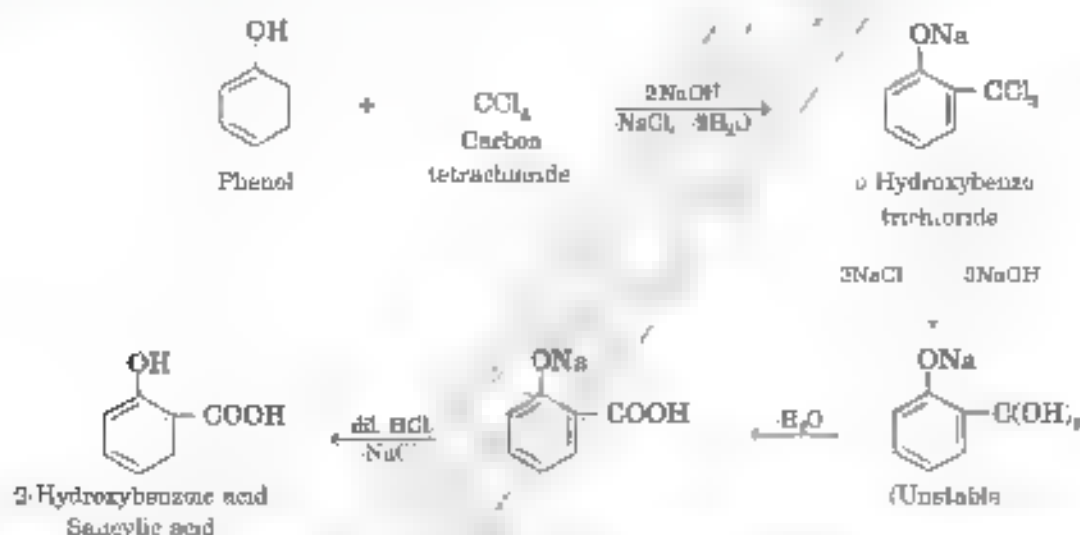
The Reimer-Tiemann reaction involves electrophilic substitution reaction. In this case the electrophile is dichlorocarbene CCl_2 . This is generated by the reaction of chloroform CHCl_3 and NaOH as



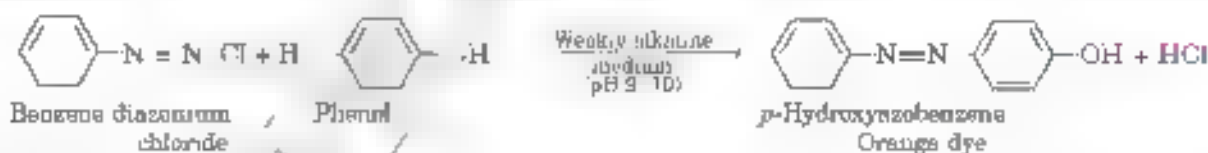
Dichlorocarbene contains carbon atom with sextet of electrons and hence is a strong electrophile. The electrophilic substitution reaction occurs as



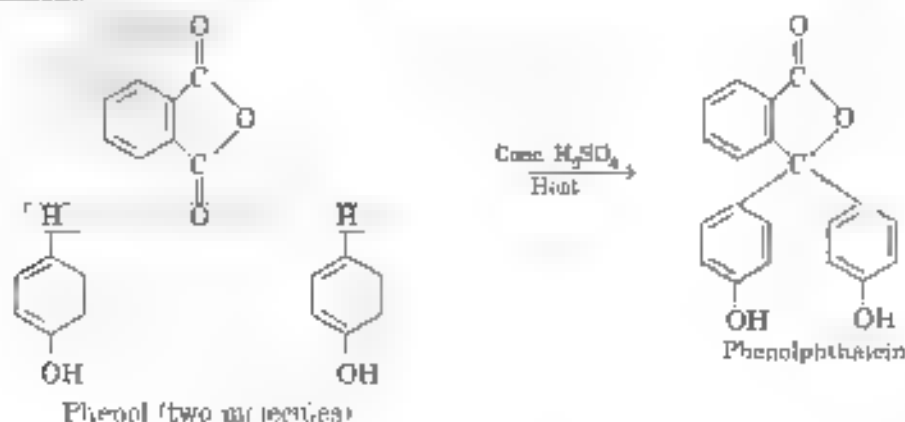
In Reimer-Tiemann reaction, carbon tetrachloride may also be used in place of chloroform. In this case *o*-salicylic acid is formed as the major product.



3. Coupling reaction. In the alkaline medium, an ice-cold solution of phenol combines with an ice-cold solution of benzene diazonium chloride to form coloured azo dyes. This reaction is called **coupling reaction**.

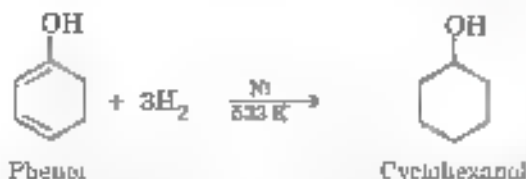


4. Reaction with phthalic anhydride. Phenol reacts with phthalic anhydride in the presence of conc. H_2SO_4 to give phenolphthalein.

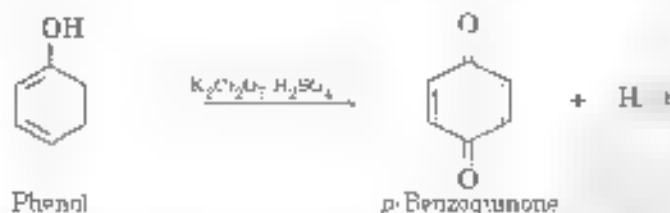


5. **Condensation with formaldehyde.** Phenol condenses with formaldehyde in the presence of dil. acid or alkali as catalyst to give a cross-linked polymer called bakelite. This reaction has been discussed in detail in Unit 15.

6. **Hydrogenation or reduction.** Phenol can be hydrogenated in the presence of finely divided nickel catalyst at 533 K to give cyclohexanol.

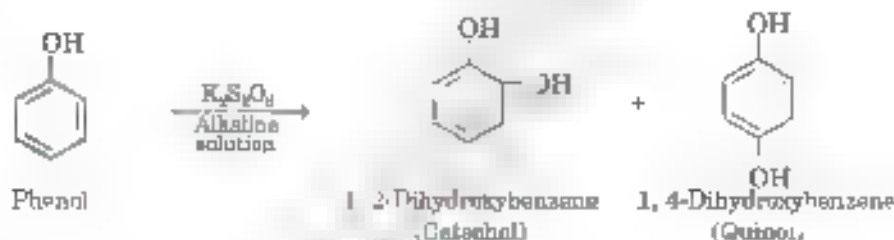


7. **Oxidation.** Phenol undergoes oxidation with chromic acid and produces a conjugated diketone known as *p*-benzoquinone.



When exposed to air, phenols are slowly oxidised to dark coloured mixtures containing *q* quinones.

Phenol can also be oxidised by potassium per sulphate, $\text{K}_2\text{S}_2\text{O}_8$, in alkaline solution and gives a mixture of catechol and quinol.



This reaction is called **Elbs persulphate oxidation**.

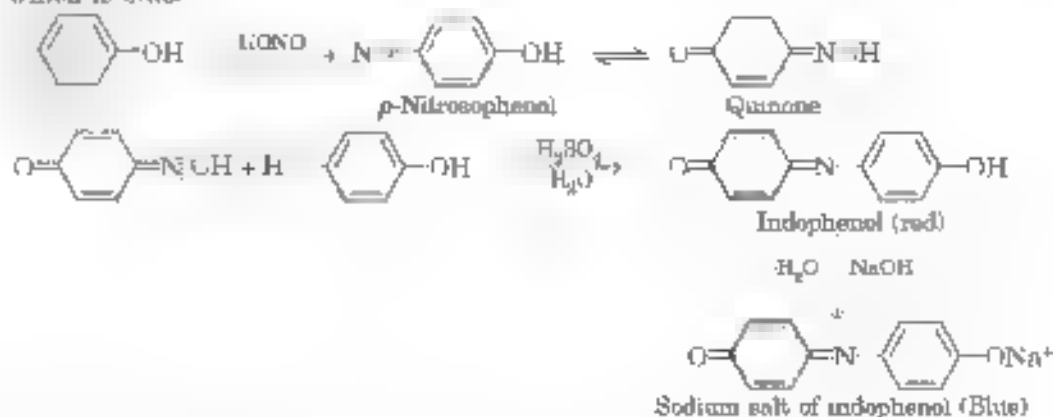
8. **Reaction with ferric chloride.** Phenols react with neutral ferric chloride to form coloured water soluble complex compounds. Different phenols give different colours (violet, red, green, blue, etc.) and therefore, this reaction serves as a test for phenols.



In fact, all compounds containing *enolic* group $=\text{C}-\text{OH}$, give this test.

9. **Liebermann's test** Most of the phenols give this test. On warming with conc. H_2SO_4 and sodium nitrite, phenols give red or brown colouration. The colour changes to blue or green by the addition of aqueous NaOH .

Phenols react with nitrous acid to give *p*-nitrosophenol which rearranges to quinone. In the presence of conc. H_2SO_4 , quinone condenses with phenol to give indophenol which is red. With excess of NaOH , sodium salt of indophenol is obtained which is blue.



This test can be used to distinguish phenols from alcohols.

DISTINCTION BETWEEN PRIMARY SECONDARY AND TERTIARY ALCOHOLS

Primary, secondary and tertiary alcohols can be distinguished by the following tests/reactions.

1. Lucas test In this test, an alcohol is treated with an equimolar mixture of concentrated hydrochloric acid and anhydrous $ZnCl_2$, called *Lucas reagent*. The alcohols get converted into alkyl chlorides. Since the alkyl chlorides are insoluble in water, their formation is indicated by the *appearance of turbidity* in the reaction mixture. Since the order of reactivity of alcohols with halogen acids is *tertiary > secondary > primary*, the time required for the appearance of cloudiness will be different in different alcohols and this test helps to distinguish them from one another.



- If turbidity appears **immediately** the alcohol is **tertiary**
- If turbidity appears **within five minutes**, the alcohol is **secondary**
- If turbidity appears **only upon heating**, the alcohol may be **primary**

2. Victor Meyer's test. This test involves the following steps:

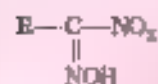
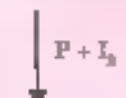
The given alcohol is treated with red phosphorus and iodine resulting in the formation of corresponding alkyl iodide.

- The alkyl iodide is treated with silver nitrate to form corresponding nitroalkane.
- The nitroalkane is finally reacted with nitrous acid, i.e. $NaNO_2$ + dil. H_2SO_4 , and the resulting solution is made alkaline.

- Formation of a **blood red colour** shows the original alcohol to be **primary**.
- Formation of a **blue colour** shows the original alcohol to be **secondary** while
- A **colourless solution** means that the alcohol is a **tertiary alcohol**.

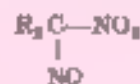
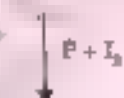
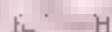
The different reactions taking place are shown below:

Primary alcohol



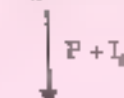
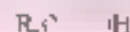
Nitrolic acid
blood red colour
when made alkaline

Secondary alcohol



Pseudo nitrol
blue colour
with alkalis

Tertiary alcohol



No action

Colourless solution

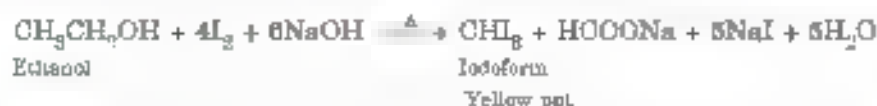
The primary, secondary and tertiary alcohols can also be distinguished by the following tests which have already been discussed:

3. Oxidation reaction (Property C. 2)
4. Reduction with copper metal at 573 K (Property C. 3).
5. **Iodoform Test**



All alcohols containing $\begin{array}{c} OH \\ | \\ CH_3CH- \end{array}$ group (linked to carbon or hydrogen atom i.e. methyl carbinols) can be distinguished from other alcohols by iodoform test. This test is performed by heating the alcohol with aqueous $NaOH$.

or Na_2CO_3 and iodine solution. On warming the reaction mixture, yellow precipitate of iodoform indicates positive iodoform test. For example, ethanol gives iodoform test as



However, methanol does not have $\text{CH}_3-\overset{\text{OH}}{\underset{|}{\text{CH}}}$ group and therefore, does not give iodoform test

$$\text{CH}_3\text{OH} + \text{I}_2 + \text{NaOH} \xrightarrow{\Delta} \text{No reaction}$$

Methanol

OH

Thus the alcohols containing CH_2-CH group give positive iodoform test. Therefore iodoform test can be used to distinguish between

- Ethanol ($\text{CH}_3\text{CH}_2\text{OH}$) and methanol (CH_3OH)
Ethanol gives this test.
- Ethanol ($\text{CH}_3\text{CH}_2\text{OH}$) and propanol ($\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$)
Ethanol gives this test.
- Propan-2-ol ($\text{H}_3\text{C}-\underset{\text{OH}}{\overset{|}{\text{CH}}}-\text{CH}_3$) and propan-1-ol ($\text{H}_3\text{C}-\text{CH}_2-\text{CH}_2\text{OH}$)
 $\text{H}_3\text{C}-\underset{\text{OH}}{\overset{|}{\text{CH}}}-\text{CH}_3$
Propan-2-ol gives this test.

$$\text{CH}_3\text{CH}(\text{OH})\text{CH}_3 + 4\text{I} + 6\text{NaOH} \xrightarrow{\Delta} \text{CHI}_3 + \text{H}_3\text{COONa} + 5\text{NaI} + 5\text{H}_2\text{O}$$

Yellow ppt

$$\text{CH}_3\text{CH}_2\text{CH}_2\text{OH} + \text{I}_2 + \text{NaOH} \xrightarrow{\Delta} \text{No reaction}$$

Propan-1-ol
- Butan-2-ol ($\text{CH}_3\text{CH}_2\underset{\text{OH}}{\overset{|}{\text{CH}}}\text{CH}_3$) and butan-1-ol ($\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$)
 $\text{CH}_3\text{CH}_2\underset{\text{OH}}{\overset{|}{\text{CH}}}\text{CH}_3$
Butan-2-ol gives this test.

$$\text{CH}_3\text{CH}_2\underset{\text{OH}}{\overset{|}{\text{CH}}}\text{CH}_3 + 4\text{I} + 6\text{NaOH} \xrightarrow{\Delta} \text{CHI}_3 + \text{CH}_3\text{CH}_2\text{COONa} + 5\text{NaI} + 5\text{H}_2\text{O}$$

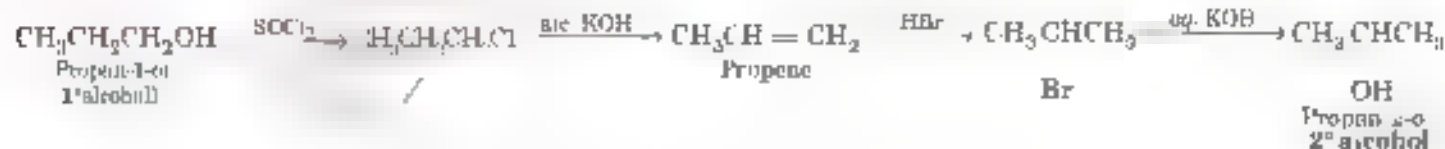
Yellow ppt

$$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH} + \text{I}_2 + \text{NaOH} \xrightarrow{\Delta} \text{No reaction}$$

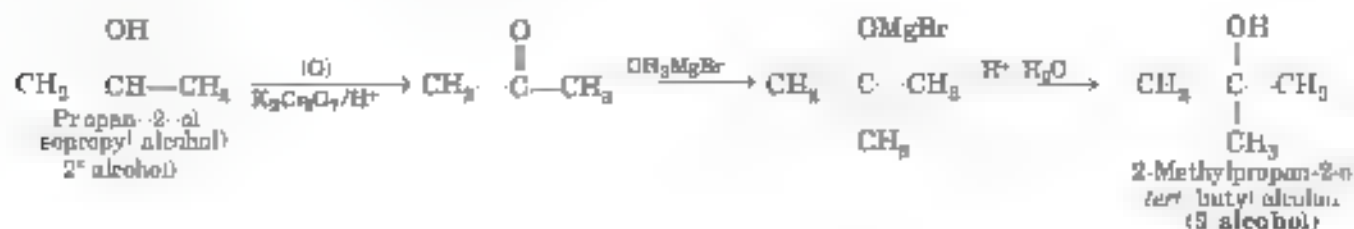
Butan-1-ol

INTERCONVERSIONS OF ALCOHOLS

(a) Primary alcohol into secondary alcohol. For example,



(b) Secondary alcohol into tertiary alcohol.



$$\begin{array}{ccccccc} \text{CH}_3 & & \text{CH}_3 & & \text{CH}_3 & & \text{CH}_3 \\ | & & | & & & & | \\ \text{CH}_3\text{CHCH}_2\text{OH} & \xrightarrow[\text{Dehydration}]{\text{H}_2\text{SO}_4, \text{Heat}} & \text{CH}_3\text{C}=\text{CH}_2 & \xrightarrow[\text{Markovnikov's rule}]{\text{HBr}} & \text{CH}_3\text{C}-\text{CH}_2\text{Br} & \xrightarrow{\text{aq. KOH}} & \text{CH}_3\text{C}-\text{CH}_2\text{OH} \\ \text{2-Methylpropan-1-ol} & & & & & & \text{2-Methylpropan-1-ol} \end{array}$$
$$\text{CH}_3\text{OH} \xrightarrow{\text{H}_1} \text{CH}_3\text{I} \xrightarrow{\text{KCN}} \text{CH}_3\text{CN} \xrightarrow[\text{Reduction}]{\text{+ H}} \text{CH}_3\text{CH}_2\text{NH}_2 \xrightarrow{\text{HONO}} \text{CH}_3\text{CH}_2\text{NH} \cdot \text{H}$$

Methanol (1° carbon atom) Ethanol (2° carbon atom)

$$\begin{array}{l} \text{CH}_3\text{CH}_2\text{OH} \xrightarrow{\text{K}_2\text{Cr}_2\text{O}_7, \text{H}^+} \text{CH}_3\text{CHO} \xrightarrow{\text{O}} \text{CH}_3\text{COOH} \xrightarrow{\text{NaOH}} \text{CH}_3\text{COONa} \\ \text{Ethanol} \qquad \qquad \qquad \text{2 carbon aldehyde} \qquad \qquad \qquad \text{Acetic acid} \qquad \qquad \qquad \text{Sodium acetate} \\ \text{2 carbon alcohol} \end{array}$$

$$\begin{array}{l} \text{CH}_3\text{OH} \xleftarrow{\text{aq. KOH}} \text{CH}_3\text{Cl} \xleftarrow{\text{Cl}_2} \text{CH}_4 \\ \text{Methanol} \qquad \qquad \qquad \text{one carbon alcohol} \end{array}$$

Alcohols and phenols can be distinguished by the following tests

Test	Phenol	Alcohol
1. Litmus test	Phenols turn blue litmus red	Alcohols do not have any effect on litmus solution.
2. With ferric chloride solution	Phenols react with neutral FeCl_3 solution to give characteristic colours blue, green, violet.	Alcohols do not give any colour with neutral FeCl_3 solution
3. Bromine water test	Phenols give white ppt. with bromine water due to the formation of 2, 4, 6-tribromophenol	Alcohols do not give white ppt. with Br_2 water
4. Coupling reaction	Phenols give coloured dye (yellow, orange or red) with cold solution of benzene diazonium chloride	Alcohols do not form any dye with benzene diazonium chloride
5. Sodium hydroxide solution	Phenols react with sodium hydroxide solution and form sodium salt	Alcohols do not react with sodium hydroxide solution
6. Liebermann's test	Phenols give red colouration on warming with sodium nitrite dissolved in conc. H_2SO_4 . The colour changes to blue on the addition of NaOH	No colour is produced.

SOLVED EXAMPLES

□ Example 6.

Arrange the following sets of compounds in order of their increasing boiling points

(a) Pentan-1-ol, butan-1-ol, butan-2-ol, ethanol, propan-1-ol, methanol.

(b) Pentan-1-ol, n-butane, pentanal, ethoxy ethane.

[N.C.E.R.T.]

Solution : Increasing order of boiling points

a. Methanol < ethanol < propan-1-ol < butan-2-ol < butan-1-ol < pentan-1-ol

b. n-Butane < ethoxy ethane < pentanal < pentan-1-ol

□ Example 8.

Name the reagents used in the following reactions

a. dehydration of propan-2-ol to propene

b. oxidation of primary alcohol to carboxylic acid

c. oxidation of primary alcohol to an aldehyde

d. butan-2-one to butan-2-ol

(e) cyclohexanone to 1-ethylcyclohexanol

Solution : a. 85% H_2SO_4 , 443 K b. alkaline KMnO_4 c. PCC d. NaBH_4 e. $(\text{CH}_3\text{CH}_2\text{MgBr})$, ether, H_3O^+

□ Example 7.

Convert phenol into

(i) Salicylaldehyde

[Hr. S.B. 2012]

(ii) Benzene

[Hr. S.B. 2012]

(iii) Picric acid

[Hr. S.B. 2012]

(iv) Benzene acid

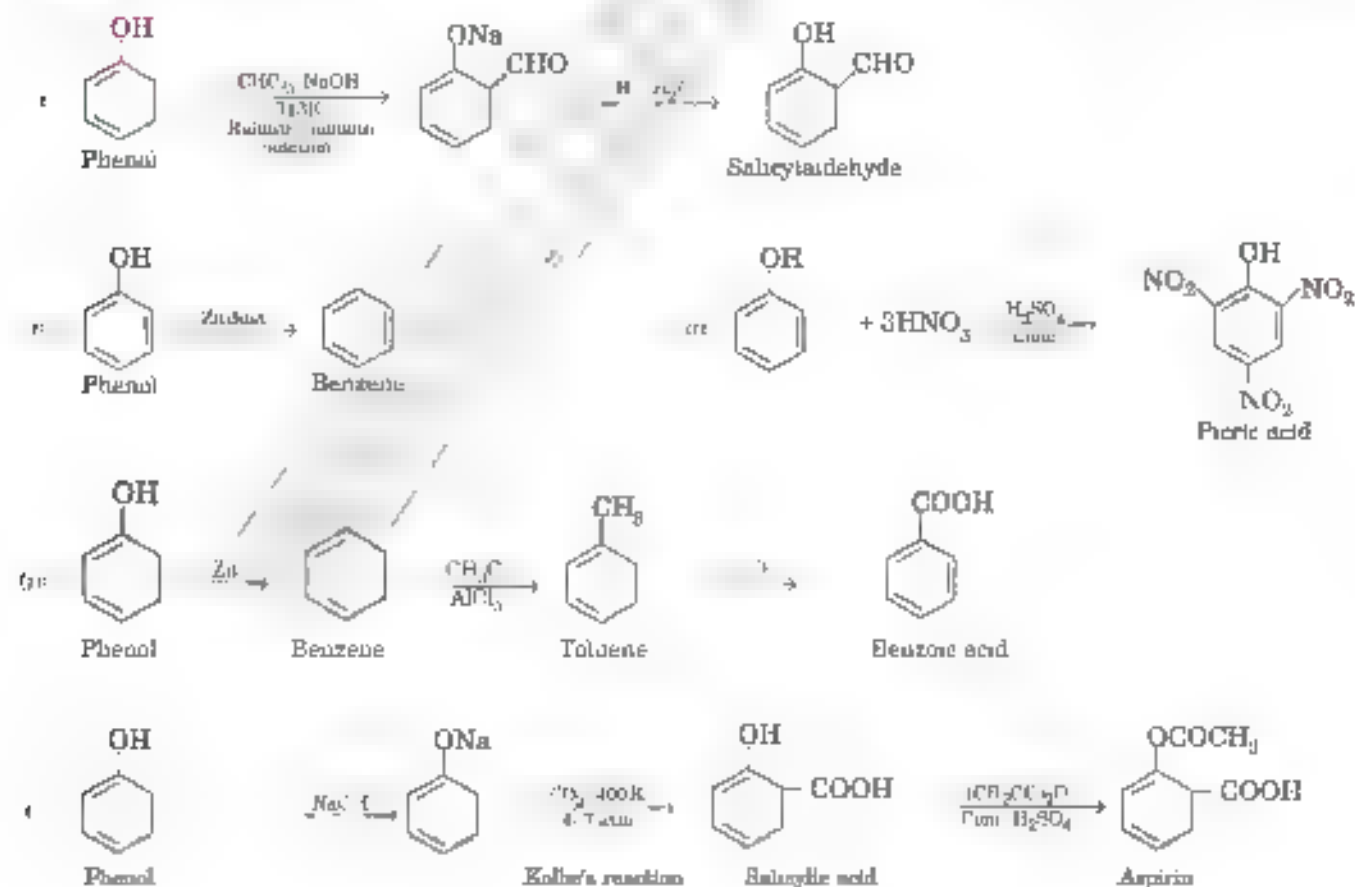
[Hr. S.B. 2005]

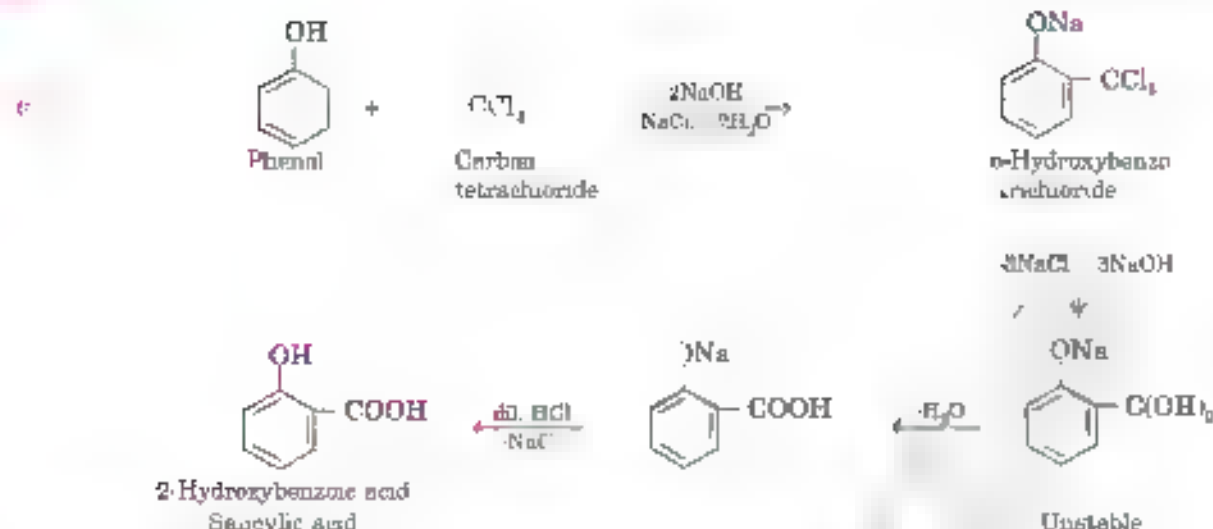
v Aspirin

[H.P. S.B. 2010S]

vi Salicylic acid [Hr. S.B. 2012, Meghalaya S.B. 2018]

Solution :





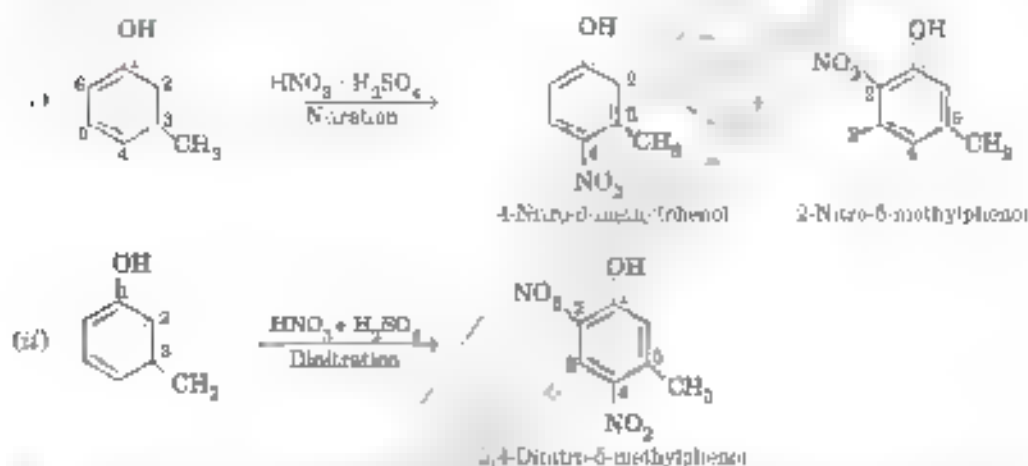
Example 8

Write the structures of the major products expected from the following reactions

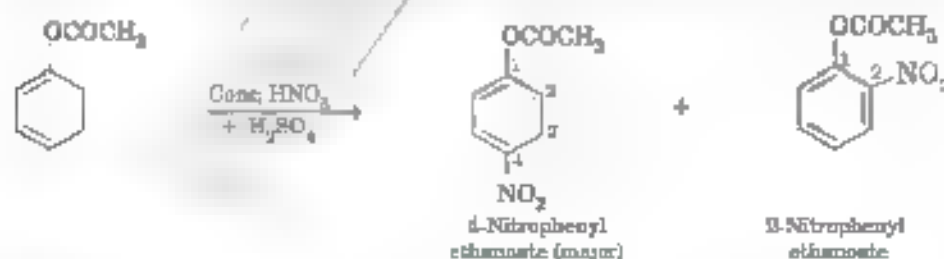
- (i) Mononitration of 3-methyl phenol (ii) Dinitration of 3-methyl phenol
 (iii) Mononitration of phenylethanone

[N.C.E.R.T.]

Solution Both OH and CH_3 groups are *o*- and *p*-directing. Therefore, position 2, 4 and 6 are activated. But due to steric hindrance, substitution does not occur at position 2, i.e., in between two groups.

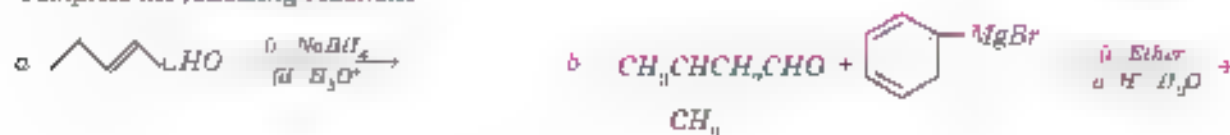


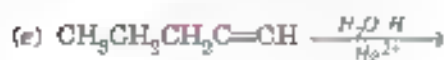
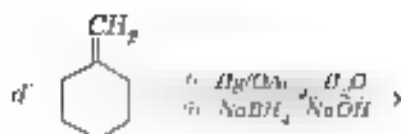
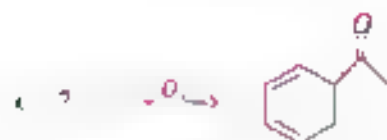
- (iv) OCOCH_3 is *o*, *p*-directing group. Due to steric hindrance, *p*-product predominates



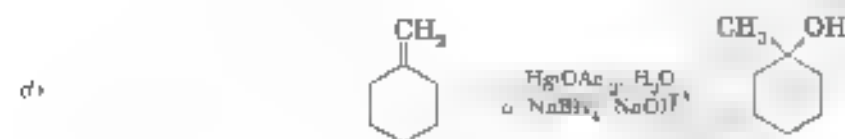
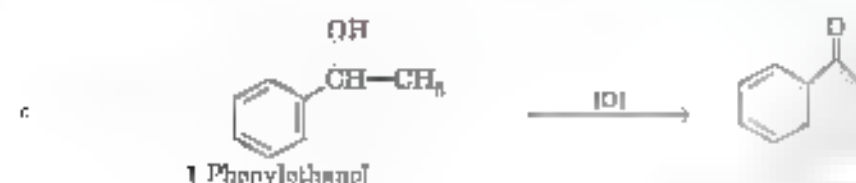
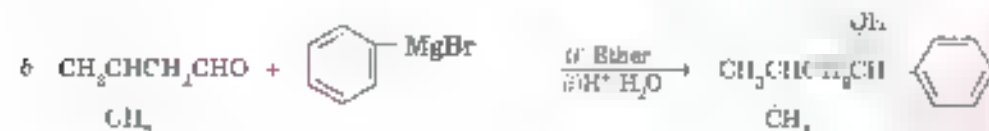
Example 9

Complete the following reactions





Solution



NOTE

Oxymercuration reduction proceeds according to Markovnikov rule

Example 10

a Arrange the following compounds in the increasing order of their acid strength
p-cresol, p-nitrophenol, phenol

b Write the mechanism, using curved arrow notation, of the following reaction.



Or

Write the structures of the products when butan-2-ol reacts with following

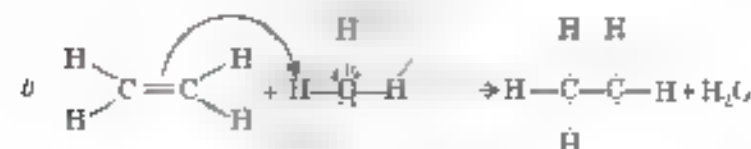
a CrO_3

b SOCl_2

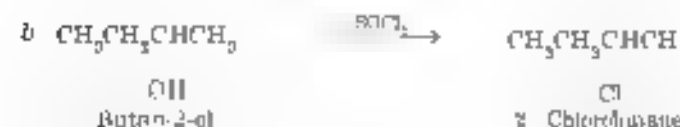
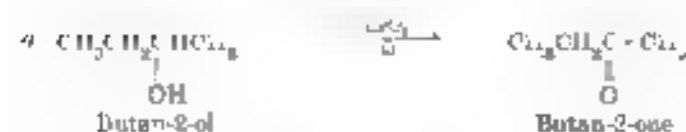
A.I.R.B. 2017

Solution

a p-cresol < phenol < p-nitrophenol



Or



Example 11.

How are the following conversions carried out ?

(i) Benzyl chloride to benzyl alcohol

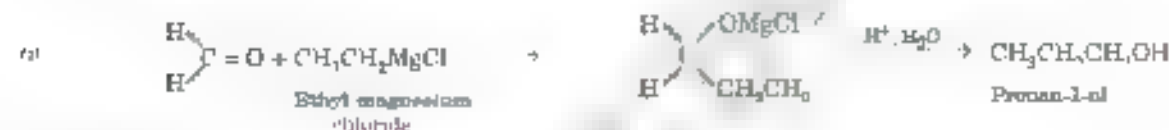
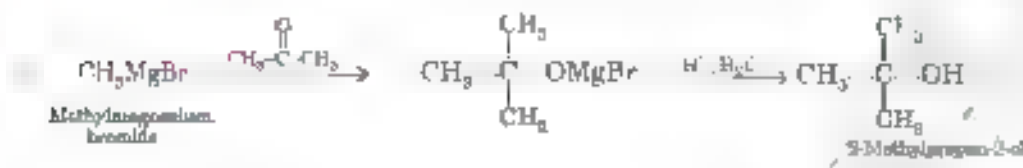
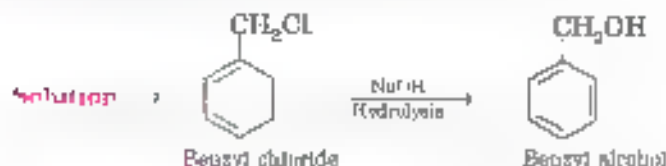
(Hr. S.B. 2018.

(ii) Methylmagnesium bromide to 2-methylpropan-2-ol.

(iii) Propene to propan-2-ol

(iv) Ethylmagnesium chloride to propan-1-ol

(D.S.B. 2010, 2019 Hr. S.B. 2018.

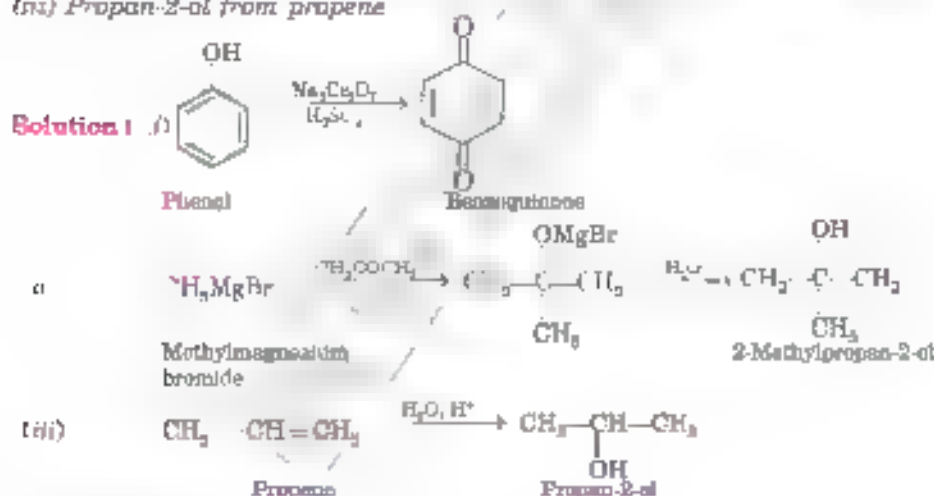
**Example 12.**

How would you obtain the following

(i) Benzophenone from phenol (ii) 2-Methylpropan-2-ol from methylmagnesium bromide

(iii) Propan-2-ol from propene

(A.I.S.B. 2011.

**Example 13.**

How will you convert

(i) Propene to propan-2-ol

(ii) Phenol to 2, 4, 6-trinitrophenol

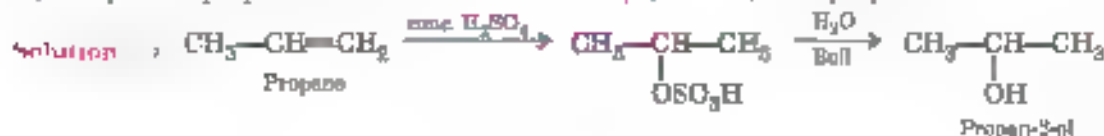
(iii) Propan-2-ol to propanone

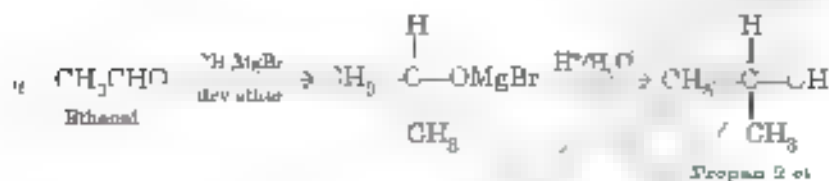
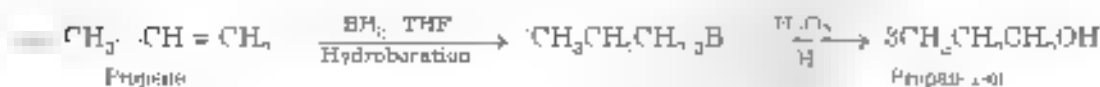
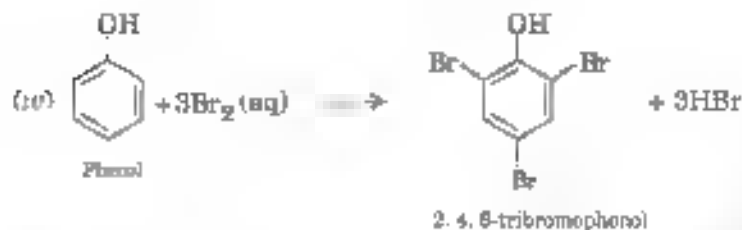
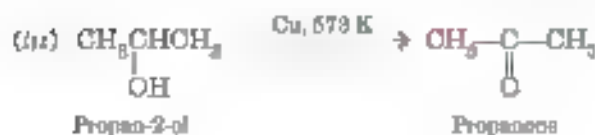
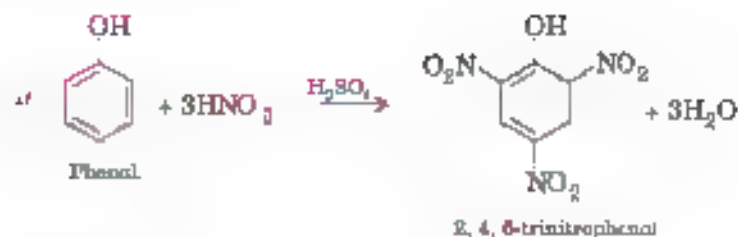
(iv) Phenol to 2, 4, 6-tribromophenol

(v) Propene to propan-1-ol

(vi) Ethanol to propan-2-ol

(D.S.B. 2013





Example 14

How will you convert

- Propan-2-ol to 3-methylpropan-2-ol
- Aniline to phenol
- Ethanol to propanenitrile
- Phenol to toluene
- Formaldehyde to ethanol

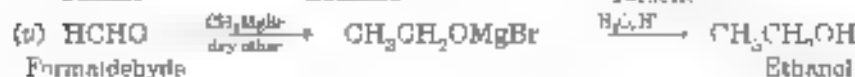
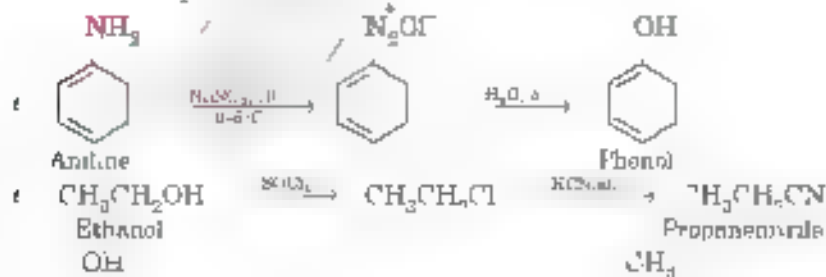
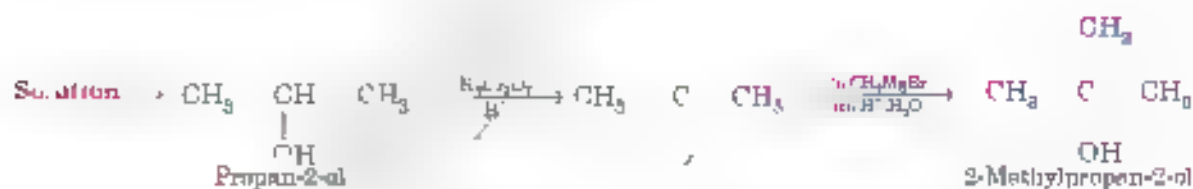
(D S.B. 2018)

(D S.B. 2018)

(A.I.S.B. 2018)

(A.I.S.B. 2018)

(A.I.S.B. 2018)



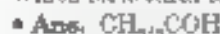
Practice Problems

7. Give the structural formulae and IUPAC names of the isomers with the molecular formula C_3H_8O . Arrange them in increasing order of their boiling point.

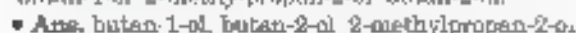


The increasing order of boiling point $(iii) < (ii) < (i)$.

8. Which structural isomer of $C_4H_{10}O$ cannot be dehydrogenated by copper at 573 K?



9. Arrange the following in order of decreasing reactivity towards Lucas reagent: butan-1-ol, 2-methylpropan-2-ol, butan-2-ol.



10. What is the major product when butan-2-ol is heated with H_2SO_4 at 443 K?



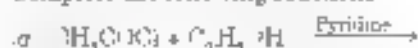
11. What products are obtained when ethyl alcohol is treated with H_2SO_4 at 443 K, 413 K and at 383 K?



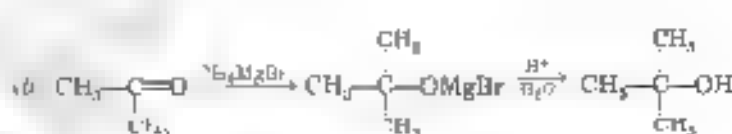
12. What happens when tert-butyl alcohol is treated with reduced copper at 573 K?



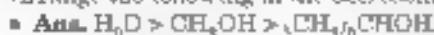
13. Complete the following reactions



• Ans.



14. Arrange the following in the decreasing order of acidic strength: H_2O , CH_3OH , CH_3CH_2OH .



15. What is the main product formed when phenol is subjected to Kolbe's reaction?



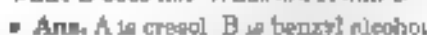
16. Arrange the following in the increasing order of acidic strength: phenol, ethanol, o-nitrophenol.



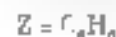
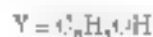
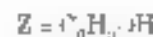
17. What happens when phenol is hydrogenated?



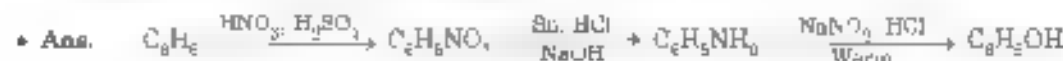
18. Two isomeric aromatic compounds A and B have the molecular formula C_7H_7OH . A gives purple colour with $FeCl_3$ solution while B does not. What are A and B?



19. Identify X, Y and Z in the following reactions



20. Give a method of converting benzene to phenol via nitrobenzene.

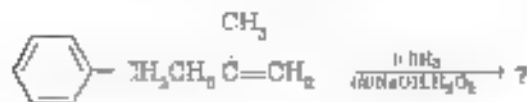


21. Predict which is stronger acid in each of the following pairs

- a. Phenol or cyclohexanol
 b. Phenol or *p*-nitrophenol
 c. *p*-Nitrophenol or *p*-chlorophenol
 d. 2, 4, 6-Trinitrophenol or 2, 4-dinitrophenol
 e. *p*-Cyanophenol or phenol
 f. $(\text{CH}_3)_3\text{CHOH}$ or $(\text{CF}_3)_3\text{CHOH}$
 g. Phenol or benzyl alcohol

• **Ans.** a. Phenol b. *p*-Nitrophenol c. *p*-Nitrophenol d. 2, 4, 6-Trinitrophenol e. *p*-Cyanophenol
 f. $(\text{CF}_3)_3\text{CHOH}$ g. Phenol

22. Predict the product of the following reaction

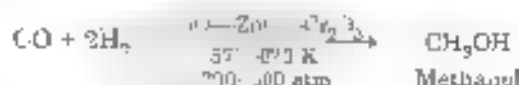


• **Ans.** $\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{OH}$ 2-Methyl-4-phenylbutan-1-ol
 (Hydroboration reaction proceeds according to anti-Markovnikov rule.)

SOME COMMERCIALY IMPORTANT ALCOHOLS

1. Methanol

Methanol or methyl alcohol is also known as *wood spirit* or *wood naphtha* because it was originally prepared by destructive distillation of wood. Nowadays, it is manufactured by catalytic hydrogenation of carbon monoxide or water gas. A mixture of carbon monoxide and hydrogen is passed over a catalyst consisting of oxides of copper, zinc and chromium at 573–673 K and under 20–200 atm pressure when methanol is formed.



Methanol is also prepared as a by-product during destructive distillation of wood.

Properties. Methanol is a colourless liquid with b.p. 337 K. It is miscible with water in all proportions. It is highly poisonous in nature and when taken internally it causes blindness or even death. It gives most of the general reactions of alcohols.

Uses of Methanol. Methanol is used

- as a solvent for paints and varnishes.
- as an antifreeze for automobile radiators.
- in the manufacture of formaldehyde which is very widely used in the manufacture of plastics.
- for denaturing ethyl alcohol i.e. to make it unfit for drinking purposes. Denatured alcohol is commonly known as methylated spirit.
- as a motor fuel.
- in the manufacture of perfumes, drugs and varnishes.

2. Ethanol

It is the most important member of the alcohol series and is simply known as **alcohol**. It is also known as **grain alcohol** because it can be prepared from starchy grains.

It can be manufactured by the following processes:

Hydration of ethene. Ethanol is prepared by the hydration of ethene at 573 K, under 200 atm pressure and in the presence of a catalyst

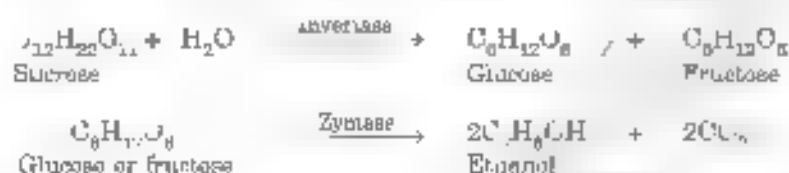


(i) **Oxo process.** Ethene reacts with carbon monoxide and hydrogen in the presence of cobalt carbonyl $(Co_2(CO)_8)$ as catalyst at high temperature and pressure to give aldehydes. The catalytic hydrogenation of aldehydes gives primary alcohols.



(ii) **Fermentation of carbohydrates.** Ethanol is manufactured by fermentation of starch or sugar. Fermentation is a process in which complex organic compounds are broken down into simpler molecules by the action of biological catalysis known as **enzymes**. **Enzymes are complex organic compounds which act as catalysts in reaction taking place in living organisms.** These are also called **bio-catalysts**.

(a) **Ethanol from sugar solution (molasses).** Molasses is a non-crystalline form of sugar obtained as the mother liquor after crystallisation of sugar from sugar solution. This contains about 50% sugar. It is diluted to about 10% solution and yeast is added and kept for about 2-3 days. Yeast supplies the enzymes **invertase** and **zymase**. The enzyme **invertase** hydrolyses sucrose to glucose and fructose. The enzyme **zymase** found in yeast converts glucose and fructose to ethanol.

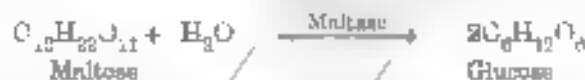


The fermented liquid which contains about 8-10% ethanol is called **wash**. It is fractionally distilled to rectified spirit containing 95.0% alcohol. Further dehydration with quick lime and **distilling** with sodium or calcium gives 99.8% ethanol.

(b) **Ethanol from starch.** Ethanol is also prepared industrially from starchy substances like potato, barley, yam, etc. Starchy substances are made into a paste by heating with super-heated steam at about 335 K and malt is added. The malt contains the enzyme **diastase** which converts starch into maltose.



The product is cooled to about 305K and yeast is added. It gives enzyme **maltase** which converts maltose to glucose.



The enzyme **zymase** also provided by yeast converts glucose into ethanol.



In wine making, grapes are the source of sugars and yeast. As grapes ripen the quantity of sugar increases and the yeast grows on the skin of the grapes. When the grapes are crushed, sugar and enzyme come in contact and fermentation starts. Fermentation takes place under **anaerobic conditions** i.e. in the absence of air. During fermentation CO_2 is released.

The action of enzyme is inhibited when the concentration of alcohol exceeds 14%. If air enters the fermentation mixture, the O_2 of the air oxidises ethanol to ethanoic acid which spoils the taste of alcoholic drinks and makes it sour.

Properties. It is a colourless, volatile liquid with characteristic pleasant odour. It has boiling point of 351K. It gives all general reactions of alcohols.

Uses of Ethanol. Ethyl alcohol is used

- (i) as an industrial solvent for paints, lacquers, dyes, varnishes, cosmetics, perfumes, etc.
- (ii) in the manufacture of alcoholic beverages.
- (iii) in the preparation of ether, chloroform, iodoform, acetaldehyde, acetic acid, etc.
- (iv) in scientific instruments such as thermometers and spirit levels.
- (v) as an antifreeze in automobile radiators.
- (vi) as a preservative for biological specimens.

- (iii), as a fuel in spirit lamps and stoves.
- (iv), in hospitals as an antiseptic
- (v) in the manufacture of drugs, flavouring extracts, perfumes, etc.

1. Industrial Alcohols

Ethyl alcohol is one of the most important raw materials which is quite frequently used. It is sold in different grades of purity for different purposes. These are described below.

Absolute alcohol. It is 100% pure ethanol. The fermentation of carbohydrates gives ethanol containing water. The fractional distillation of aqueous solution of ethanol gives a constant boiling azeotropic mixture which contains 95% ethanol. To get 100% ethanol a small amount of benzene is added with azeotropic mixture and then distilled. The first fraction at 347.8 K consists of water, ethanol and benzene. After water is removed, the second fraction at 341.2 K consists of benzene and ethanol. Finally pure ethanol is distilled at the azeotropic fraction, 351.2 K.

Methylated spirit or denatured alcohol. It is 95% ethyl alcohol. To avoid the misuse of alcohol meant for industries for drinking purposes it is made unfit by mixing in it methanol, some copper sulphate to give it a colour and pyridine (a foul smelling liquid), etc. The process is called denaturation of alcohol and the alcohol thus obtained, is called methylated spirit or denatured alcohol. It is quite cheap and can be used for non-drinking purposes and particularly in industries.

Power alcohol. It is a mixture of 20% ethanol and 80% gasoline. Since alcohol does not mix with petrol, therefore a third solvent such as benzene, ether or tetrahydrofuran is added. Due to the increased world consumption of petrol and its limited natural sources, petrol generally remains in a short supply. The use of power alcohol as a substitute for gasoline has promised bright future in India because we can manufacture large quantities of alcohol from molasses.

Alcoholic beverages. Liquors used for drinking purposes contain alcohol as the principal intoxicating agent. These are also called **alcoholic beverages**. They are prepared from different substances and contain different percentages of alcohol. There are mainly two types of beverages, *strong* and *weak*. Undenatured beverages are prepared from grapes and other fruit juices and are called *wines*. The liquors obtained by distillation have higher alcohol contents and have different trade names such as *whisky, rum, brandy, gin*, etc.

Toxicity of Alcohols

The toxicity of alcohols is mainly due to their oxidation to aldehydes taking place in living organisms. Methyl alcohol is highly toxic and its consumption causes blindness and death. Ethyl alcohol is non-toxic but produces physiological effects disturbing many activities in living. The commercial alcohol is made unfit for drinking by adding a copper sulphate which gives it a blue colour. Pyridine which makes it a foul smelling liquid, it is known as denaturation. In alcohol

4. Phenol or Carboic acid

Phenol was first isolated from coal tar. Nowadays, it is manufactured by Dow's process from chlorobenzene or by cumene process.

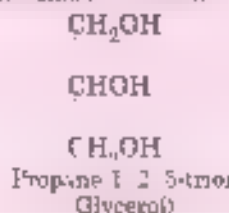
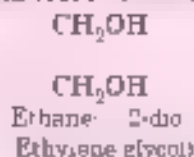
It is colourless, hygroscopic, crystalline solid. Its melting point is 315 K and boiling point is 455 K. The liquid form of phenol containing about 5% water is known as *carbolic acid*. It turns pink on exposure to air and light.

Uses of Phenol. Phenol is used

- (i) for the manufacture of bakelite by polymerizing with formaldehyde
- (ii) in the manufacture of drugs like aspirin, salol, phenacetin, etc.
- (iii) as an antiseptic in soaps, lotions, etc.
- (iv) for preparing phenolphthalein used as an indicator in acid-base titrations
- (v) as a preservative for ink
- (vi) for the manufacture of cyclohexanol used as a solvent for rubber and lacquers.
- (vii) in the manufacture of azo dyes.
- (viii) in the manufacture of picric acid used in making explosives.

POLYHYDRIC ALCOHOLS

In addition to monohydric alcohols, two polyhydric alcohols are also commercially important. These are the compounds which contain two or more hydroxy groups $-OH$ in the molecule. The compounds which contain two $-OH$ groups are called **diols**. Their IUPAC names are obtained by adding the suffix **diol** to the name of the parent alkane. The compounds containing three $-OH$ groups are called **triols**. Their IUPAC names are obtained by adding the suffix **triol** to the name of the parent alkane. The two common examples are



add on

Conceptual Questions 1

Q.1. Arrange the following compounds in increasing order of their acid strength

Propan-1-ol, 2, 4, 6-trinitrophenol, ultraphenol, 3, 5-dinitrophenol, phenol, 4-methylphenol. [N.C.E.R.T.]

Ans. Increasing order of acid strength is

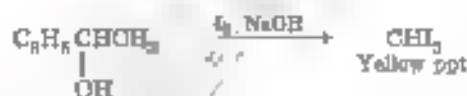
Propan-1-ol, 4-methylphenol, phenol, 3-nitrophenol, 5-nitrophenol, 3, 5-dinitrophenol, 2, 4, 6-trinitrophenol.

Q.2. In the process of wine making, ripened grapes are crushed so that sugar and enzyme should come in contact with each other and fermentation should start. What will happen if anaerobic conditions are not maintained during this process? [CBSE Sample Paper 2017-18]

Ans. Ethanol will be converted into ethanoic acid.

Q.3. How will you distinguish between 1-phenylethanol and 2-phenylethanol?

Ans. 1-Phenylethanol, $\text{C}_6\text{H}_5\text{CH}(\text{OH})\text{CH}_3$ contains the grouping $\text{CH}(\text{OH})\text{CH}_3$ and therefore will give iodoform test.



On the other hand, 2-Phenylethanol, $\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{OH}$ does not contain $\text{CH}(\text{OH})\text{CH}_3$ group and therefore it will not give iodoform test.

Q.4. Sodium metal can be used for drying diethyl ether and benzene and not ethanol.

Ans. Ethanol has a replaceable hydrogen atom and therefore reacts with sodium.



While benzene and diethyl ether do not have replaceable hydrogen atoms and hence do not react with sodium. Therefore, these can be dried by sodium metal.

Q.5. Arrange the following compounds in the order of increasing boiling points

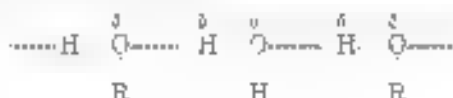
Ethanol, Propan-1-ol, Butan-1-ol, Butan-2-ol

[Kerala S.E. 2017]

Ans. Ethanol < Propan-1-ol < Butan-2-ol < Butan-1-ol

Q.6. Explain why alcohols are comparatively more soluble in water than the corresponding hydrocarbon.

Ans. The comparatively higher solubility of alcohols in water as compared to hydrocarbons is due to the formation of hydrogen bonds between alcohol and water molecules.



Q.7 Arrange the following compounds in the decreasing order of their boiling points.

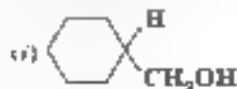
(i) Pentan-1-ol

(ii) 2-Methylbutan-2-ol

(iii) 3-Methylbutan-2-ol

Ans. $(i) > (iii) > (ii)$ This is because with branching the shape becomes spherical and therefore, van der Waals forces decrease. As a result, boiling point decreases.

Q.8. What is Jones reagent? Give the product of oxidation of



(ii) $\text{CH}_3\text{CH}=\text{CHCH}(\text{OH})\text{CH}_3$ by Jones reagent.

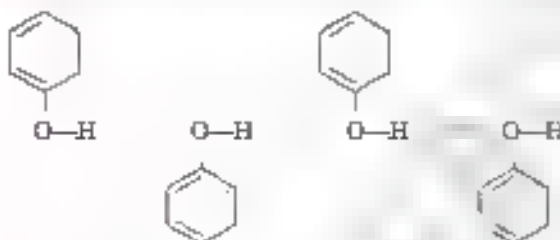
Ans. Jones reagent is CrO_3 in aqueous acetone solution. This is a mild reagent so that it oxidises alcohols without oxidising or rearranging double bonds.



Q.9. Why has phenol higher boiling point than toluene?

(Pb.S.B. 2015)

Ans. Phenol (molecular mass 94) has higher boiling point than toluene (molecular mass 92). This is due to the fact that phenol forms intermolecular hydrogen bonding leading to association of its molecules. Consequently additional energy is needed to break hydrogen bonds which raises its boiling point.



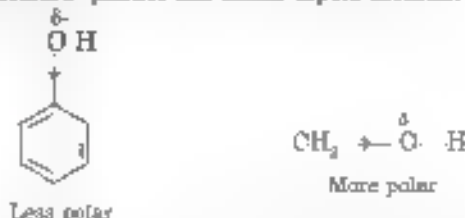
On the other hand, toluene does not form hydrogen bonds and therefore, its boiling point is less.

Q.10. Out of phenol and benzene, which is more easily nitrated and why?

Ans. Phenol can be more easily nitrated than benzene. This is because $-\text{OH}$ group is electron releasing group and it increases electron density on the benzene ring, particularly at the ortho and para positions. Since nitration involves attack of nitronium (NO_2^+) ion, its attack on phenol will be easier than on benzene where no electron releasing group is present.

Q.11. Why has phenol smaller dipole moment than methanol?

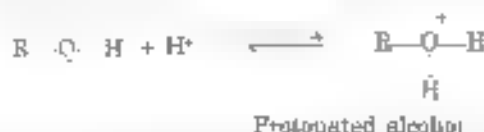
Ans. CH_3 group is electron releasing group and therefore it increases the negative charge on the oxygen atom in CH_3OH . Therefore, $\text{C}-\text{O}$ bond in it is more polar and hence methanol has high dipole moment. Phenyl group is electron attracting group and it reduces negative charge on the oxygen in $\text{C}_6\text{H}_5\text{OH}$. As a result, $\text{C}-\text{O}$ bond is less polar in phenol and therefore phenol has small dipole moment.



Q.12. Alcohols are easily protonated in comparison to phenols. Explain.

(A.I.S.B. 2016)

Ans. In alcohols, the electron releasing inductive effect (+I effect) of the alkyl group attached to the carbon having the $-\text{OH}$ group increases the electron density on the oxygen atom. Therefore, alcohols are easily protonated.



In the other hand, in the case of phenol the oxygen atom acquires a partial positive charge due to resonance. Thus, it is not protonated.

Q.13. How do you account for the fact that unlike phenol, 2,4-dinitrophenol and 2, 4, 6-trinitrophenol are soluble in aqueous sodium carbonate solution?

Ans. Nitro group is electron withdrawing group and stabilizes the phenoxide ion by dispersing the negative charge on its oxygen. As a result, the acidic strength of nitro phenols is more than that of phenol. This effect is more pronounced at *o*- and *p*-positions. Therefore 2, 4-dinitrophenol and 2, 4, 6-trinitrophenols are more acidic than phenol. As a result, they are stronger acids than carbonic acid H_2CO_3 . Hence they react with Na_2CO_3 to form their corresponding salts and dissolve in aqueous sodium carbonate solution with the evolution of CO_2 .

Q.14. Why do alcohols have higher boiling points than haloalkanes of the same molecular mass?

Ans. The boiling points of alcohols are higher than the corresponding haloalkanes of the same molecular mass. This is mainly due to strong intermolecular hydrogen bonding between alcohol molecules. Because of hydrogen bonding in alcohols, energy has to be supplied to overcome the force of attraction and consequently boiling points are high. No such hydrogen bonding exists in haloalkanes. For example, b.pt. of CH_3OH is 327.5 K while that of CH_3Cl is only 249 K .

Q.15. While separating a mixture of *ortho* and *para* nitrophenols by steam distillation, name the isomer which is more volatile. Give reason.

Ans. *Ortho* nitrophenol is more volatile. This is because it has weak intermolecular hydrogen bonding while *p*-nitrophenol is associated with strong intermolecular hydrogen bonding.

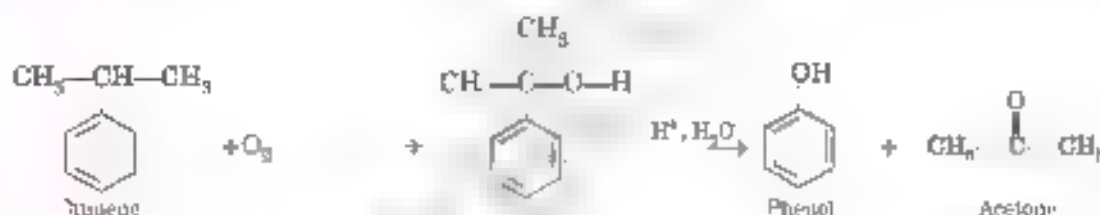
Q.16. Explain why *ortho* nitrophenol is more acidic than *ortho* methoxy phenol. *H.P.S.B. 2015, A.I.S.B. 2015,*

Ans. This is because $-\text{NO}_2$ nitro group is electron withdrawing group and will increase the +ve charge on oxygen to make it more acidic. In the other hand, $-\text{OCH}_3$ group is electron releasing group and will decrease +ve charge on oxygen making it less acidic as $\text{O}-\text{H}$ bond will not break easily.

Q.17. Write reaction for the preparation of phenol from cumene.

(Uttarakhand C.B. 2014)

Ans.

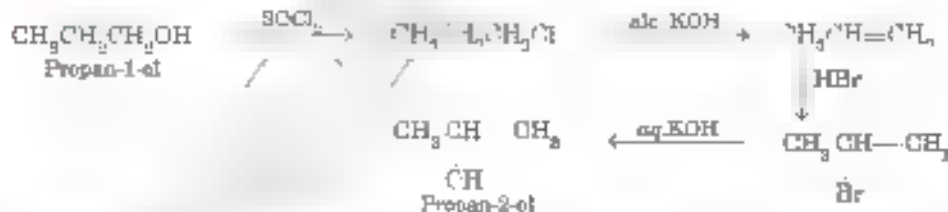


Q.18. Complete the following reactions:

(Hr. S.B. 2005)

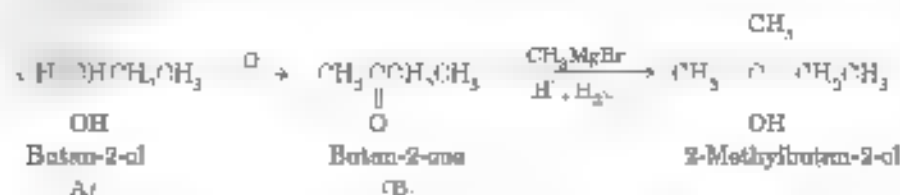


Ans.



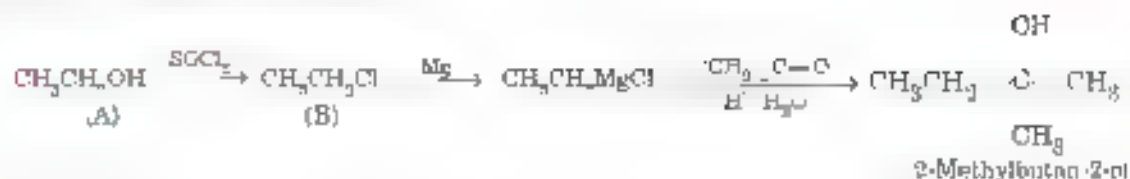
Q.19. A compound (A) with molecular formula $\text{C}_4\text{H}_{10}\text{O}$ on oxidation forms compound (B). The compound (B) gives positive iodoform test and on reaction with CH_3MgBr followed by hydrolysis gives (C). Identify A, B and C and give the sequence of reactions.

Ans. Since B gives positive iodoform test, it must be methyl ketone $\text{CH}_3\text{COCH}_2\text{CH}_3$. B will be obtained by the oxidation of 2-butanol (A). The reactions are



Q.20. A compound (A) reacts with thionyl chloride to give compound (B). B reacts with magnesium to form a Grignard reagent which is treated with acetone and the product is hydrolysed to give 2-methyl-2-butanol. What are (A) and (B) compounds?

Ans. A is ethyl alcohol B is ethyl chloride



Q.21. An alkoxide is a stronger base than hydroxide ion. Justify.

(CBSE Sample Paper 2012)

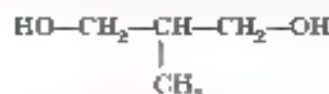
Ans. Due to the presence of electron donating alkyl group there is high electron density on alkoxide ion as compared to hydroxide ion. Therefore, alkoxide ion is more basic than hydroxide ion.

Q.22. Why is \pm butan-2-ol optically inactive?

D.S.B. 2013, A.I.S.B. 2013

Ans. \pm -Butan-2-ol represents racemic mixture of (+)-butan-2-ol and (-)-butan-2-ol which rotate the plane polarised light in different directions but to equal extent. Therefore, \pm compound is optically inactive.

Q.28. Write the EUPAC name of the given compound:



(4.9.8 8015)

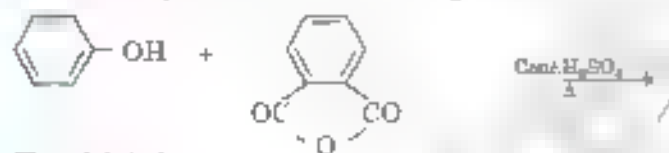
Ans. 2. Methylpropane-1, 3-diol

Q.24. Write an isomer of C_6H_5OH .

(Pb, Sn 2017)

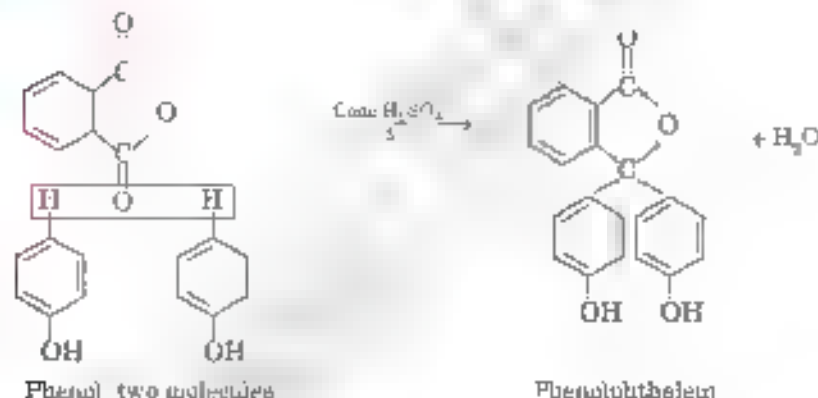
Ans. CH_3OCH_3 , Methoxymethane

Q.25. Predict the product in the following reaction:



LPG, S.H. 2015)

Ass. Theodorpalmbaum

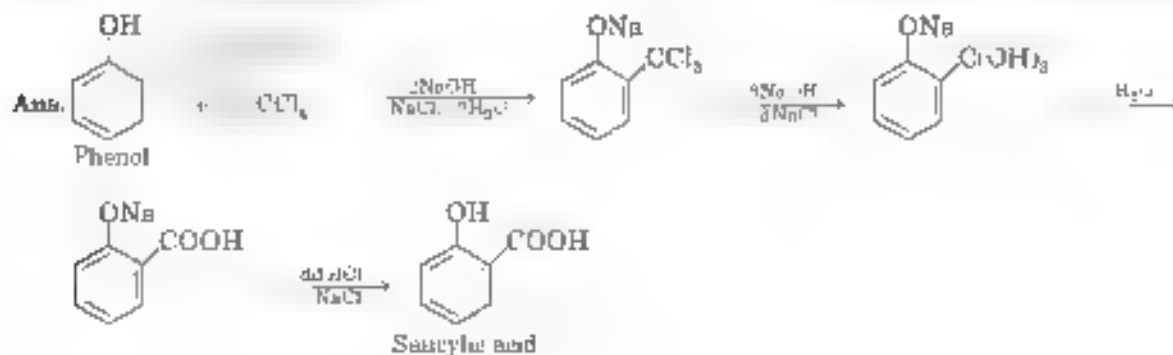


Phenyl 480 மலிவுப்பள்ள

ပြည်သူ့ပြည်တံခါး

Q.25 Convert phenol to salicylic acid.

H P S. B. 2018, Meghalaya S.B. 2018



PART B

ETHERS

Ethers are the compounds having O as the functional group. The general formula of ethers is $R-O-R$ where R may be alkyl or aryl group. Ethers may be classified as :

Aliphatic ethers in which R and R' are both alkyl groups. For example,



Dimethyl ether



Ethyl methyl ether

Aromatic ethers in which either one or both R and R' groups are aryl groups. For example,



Methyl phenyl ether



Diphenyl ether

Aromatic ethers may be further sub-divided as

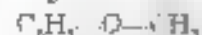
Ethers in which one of the groups is aryl while the other is alkyl are called **alkyl aryl ethers** or **phenolic ethers**.

Ethers in which both the groups are aryl are called **diaryl ethers**. For example



Dimethyl ether

(Aliphatic ether)



Methyl phenyl ether

(alkyl aryl ether)



Diphenyl ether

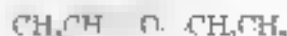
(diaryl ether)

Aromatic ethers

Symmetrical and unsymmetrical ethers. When the two aryl groups in an ether are same, the ether is said to be **symmetrical** or **simple ether**. For example



Dimethyl ether



Diethyl ether



Diphenyl ether

When the two alkyl groups in an ether are different, the ether is said to be **unsymmetrical** or **mixed ether**. For example,



Ethyl methyl ether



Methyl phenyl ether

NOMENCLATURE OF ETHERS

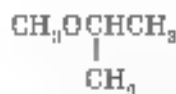
According to **common system**, ethers are named according to *alkyl group attached to the oxygen atom*. The names of the two alkyl or aryl groups linked to oxygen are written as separate words alphabetically followed by the word 'ether'. For example,



Dimethyl ether



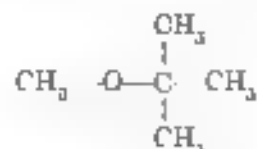
Ethyl methyl ether



Methyl isopropyl ether



Methyl phenyl ether



tert-Butyl methyl ether



Ethyl phenyl ether



Diphenyl ether

Some aromatic ethers have special common names. For example,



Anisole

Methyl phenyl ether



Phenetole

Ethyl phenyl ether

According to **IUPAC system**, ethers are named as **alkoxyalkanes**. The larger alkyl group forms the parent chain while other alkyl group is taken with the etheral oxygen and forms a part of *alkoxy group*. For example,



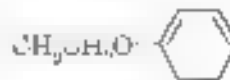
Methoxymethane



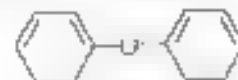
Methoxyethane



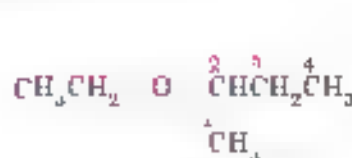
Methoxybenzene



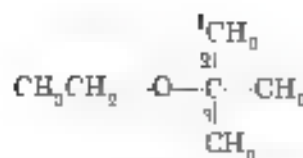
Ethoxybenzene



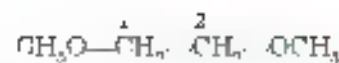
Phenoxybenzene



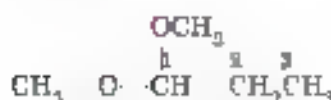
2-Ethoxybutane



3-Ethoxy-2-methylpropane



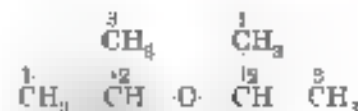
1, 2-Dimethoxyethane



1, 1-Dimethoxypropane



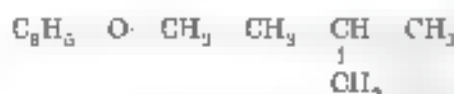
2-Methoxybutane



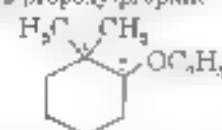
2-(2-propoxy)propane



2-Ethoxypropane

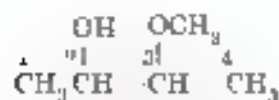


3-Methylbutoxybenzene



2-Ethoxy-1, 1-dimethylcyclohexane

If any other functional group is also present, then that group gets priority and becomes the *principal group*. For example



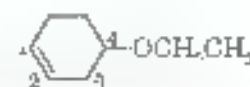
3-Methoxybutan-2-ol



2-Ethoxyethanol



Methoxyethene



4-Ethoxycyclohexene

The common and IUPAC names of some ethers are given below

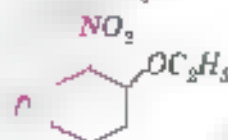
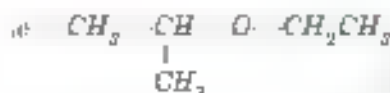
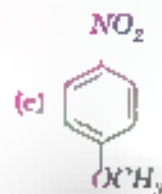
Table 1 Common and IUPAC names of some ethers.

Compound	Common name	IUPAC name
CH_3OCH_3	Dimethyl ether	Methoxymethane
$\text{C}_2\text{H}_5\text{OC}_2\text{H}_5$	Diethyl ether	Ethoxyethane
$\text{CH}_3\text{OC}_2\text{H}_5$	Ethyl methyl ether	Methoxyethane
$\text{CH}_3\text{OC}_3\text{H}_7$	Methyl n-propyl ether	1-Methoxypropane
$\text{C}_6\text{H}_5\text{OCH}_3$	Methyl phenyl ether (anisole)	Methoxy benzene
$\text{C}_2\text{H}_5\text{OC}_6\text{H}_5$	Ethyl phenyl ether (phenetole)	Ethoxybenzene
$\text{C}_6\text{H}_5\text{OC}_7\text{H}_{15}$	Heptyl phenyl ether	1-Phenoxyheptane
$\text{CH}_3\text{O}\overset{\overset{2}{\text{CH}}}{\underset{\underset{1}{\text{CH}_3}}{\text{CH}}}$	Methyl isopropyl ether	3-Methoxypropane
$\text{CH}_3-\text{OCH}_2\text{CH}_2\text{OCH}_3$		1, 2-Dimethoxyethane
$\text{C}_6\text{H}_5-\text{O}-\overset{\overset{1}{\text{CH}_2}}{\underset{\underset{2}{\text{CH}_2}}{\text{CH}}}-\overset{\overset{3}{\text{CH}}}{\underset{\underset{4}{\text{CH}_3}}{\text{CH}}}$	Isopentyl phenyl ether	3-Methylbutoxybenzene
$\text{Cl}-\overset{\overset{2}{\text{CH}_2}}{\underset{\underset{1}{\text{CH}}}{\text{C}}}-\text{CH}_2$	Epichlorohydrin	3-Chloro-1, 2-epoxypropane

SOLVED EXAMPLES

□ Example 15.

Give IUPAC names of the following



[N.C.E.R.T.]

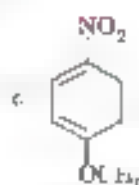
Solution: IUPAC names



1-Methoxy-2-methylpropane



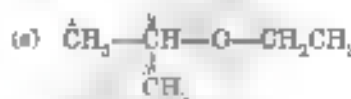
2-Chloro-1-methoxyethane



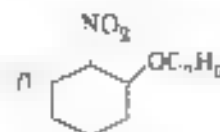
4-Nitro anisole



1-Methoxypropane



1-Ethoxypropane



1-Ethoxy-2-nitrocyclohexane

Practice Problems

23. Write the IUPAC names of the following ethers whose common names are given

Isopropyl methyl ether

Phenetole

α -chloro ethyl methyl ether

α -Cyclohexyl n -propyl ether

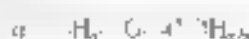
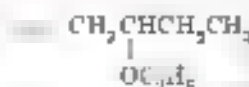
●Ans. i. 2-Methoxypropane

ii. Ethoxy benzene

iii. 1-chloro-2-methoxyethane

iv. n -propoxycyclohexane

24. Write the IUPAC names of the following



●Ans. i. 2-Ethoxybutane

ii. 2-Methoxypropane

a. 2-Methoxy-2-methylpropane

b. 1-Ethoxy-2-methoxyethane

c. Ethoxy benzene

d. Bromomethoxy benzene

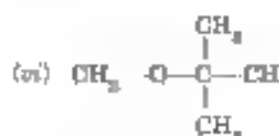
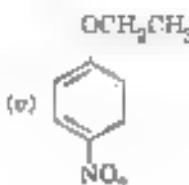
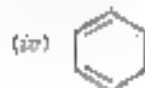
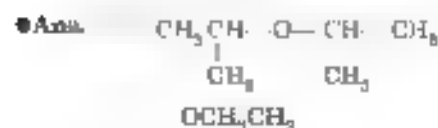
25. Write the structural formulae of the following

(i) Di-n-propyl ether

(iv) Phenetole

(ii) Dimethyl ether

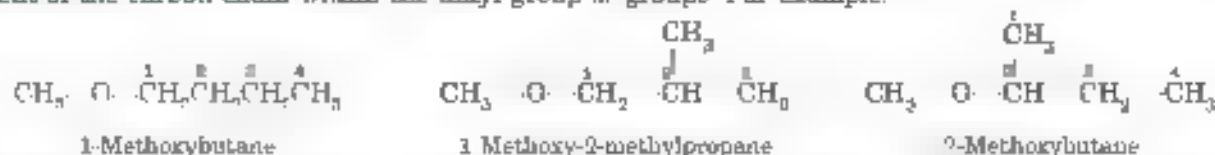
(v) p -Nitrophenetole



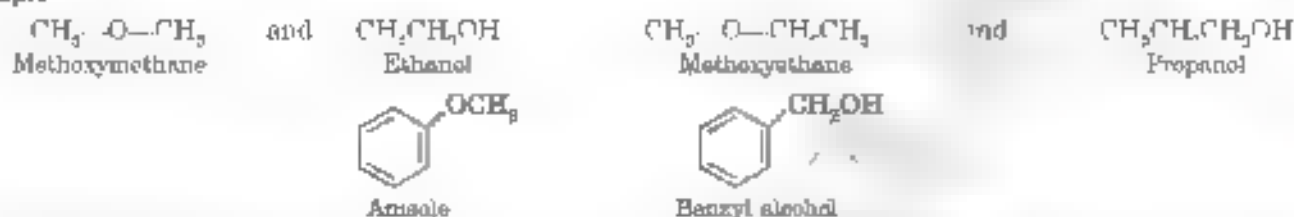
ISOMERISM IN ETHERS

Ethers show the following types of isomerism

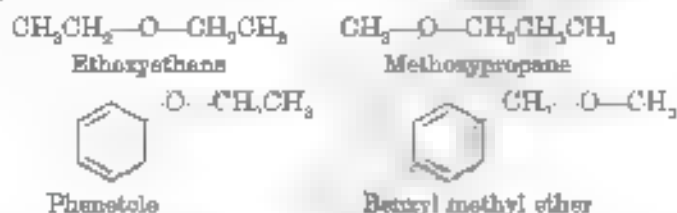
1. Chain isomerism. These have the same alkyl groups on either side of the oxygen atom but different arrangement of the carbon chain within the alkyl group or groups. For example,



2. Functional isomerism. Ethers containing two or more carbon atoms are functional isomer of alcohols. For example



3. Metamerism. These ethers have the same molecular formula but different alkyl groups on either side of the oxygen atoms. For example



STRUCTURE OF ETHERS

Ethers have structure similar to that of water, H_2O . In this case, oxygen undergoes sp^3 hybridisation, forming four sp^3 hybrid orbitals. Two of the four sp^3 hybrid orbitals of the oxygen atom overlap with sp^3 hybrid orbitals of two alkyl groups forming sigma (σ) bonds. The remaining sp^3 hybrid orbitals of oxygen contain a lone pair of electrons each as shown in Fig. 2. The C—O—C bond angle in ethers is tetrahedral angle. For example, in dimethyl ether, the C—O—C bond angle is 111.7° and C—O bond is 141 pm , which is almost same as in alcohols. The larger bond angle in ethers may be because of greater repulsive interactions between bulkier alkyl groups as compared to the smaller H-atoms in water. Thus, ethers have bent or angular structure.

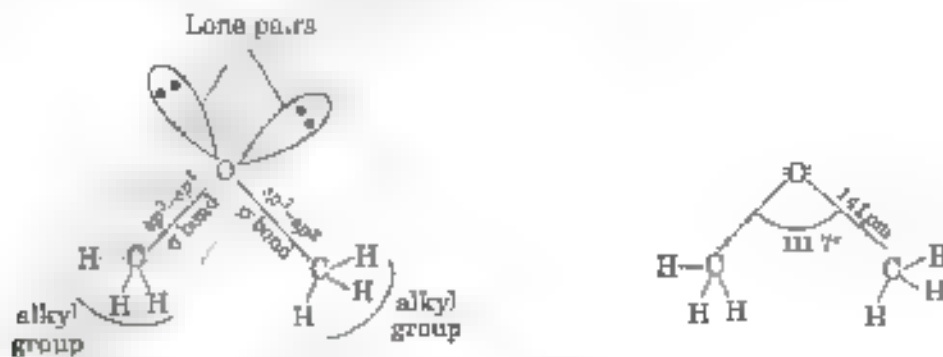


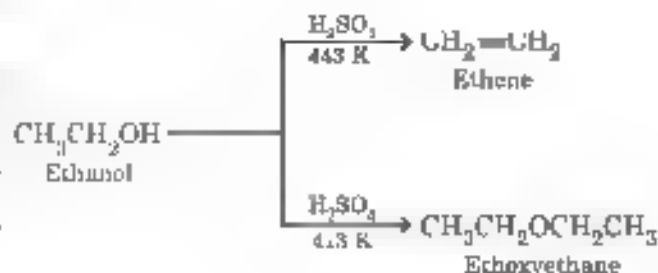
Fig. 2. Structure of dimethyl ether

METHODS OF PREPARATION OF ETHERS

Ethers can be prepared by the following general methods

1. Dehydration of alcohols

Alcohols undergo dehydration in the presence of protic acids such as H_2SO_4 , H_3PO_4 etc. to give either alkenes or ethers. The formation of product, alkene or ether depends upon the reaction conditions. For example, when ethanol is heated with conc. H_2SO_4 at 443 K , ethene is formed as the major product. However at 413 K , ethoxyethane is obtained as the major product.



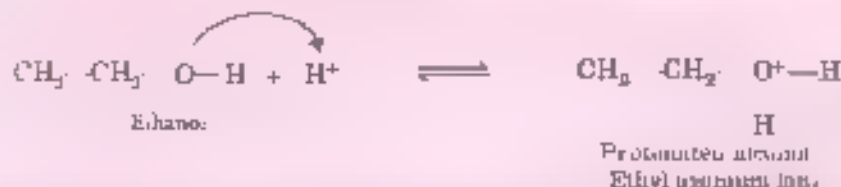
Thus, symmetrical ethers can be prepared by the dehydration of alcohols with conc. H_2SO_4 at 413 K.

The formation of ether is a nucleophilic bimolecular substitution reaction: $\text{S}_{\text{N}}2$ involving the attack of the alcohol molecule on a protonated alcohol as given below.

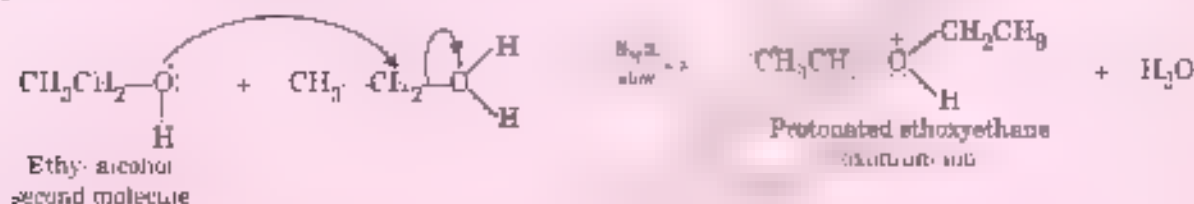
Mechanism: Formation of diethyl ether from ethanol.

The mechanism for the formation of diethyl ether from ethanol at 413 K is given below.

(i) Ethyl alcohol gets protonated in the presence of H^+



Due to the presence of a +ve charge on the oxygen atom, the carbon of CH_3CH_2 part of $\text{CH}_3\text{CH}_2\text{OH}_2^+$ becomes electron deficient. As a result, nucleophilic attack by another alcohol molecule occurs on the protonated alcohol with the elimination of a molecule of water.



(ii) Oxonium ion loses a proton to form an ether.

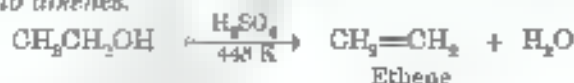


This step is fast and hence does not affect the rate of reaction.

This method is suitable for the preparation of ethers having primary alkyl groups only.

The following are some facts about the reaction.

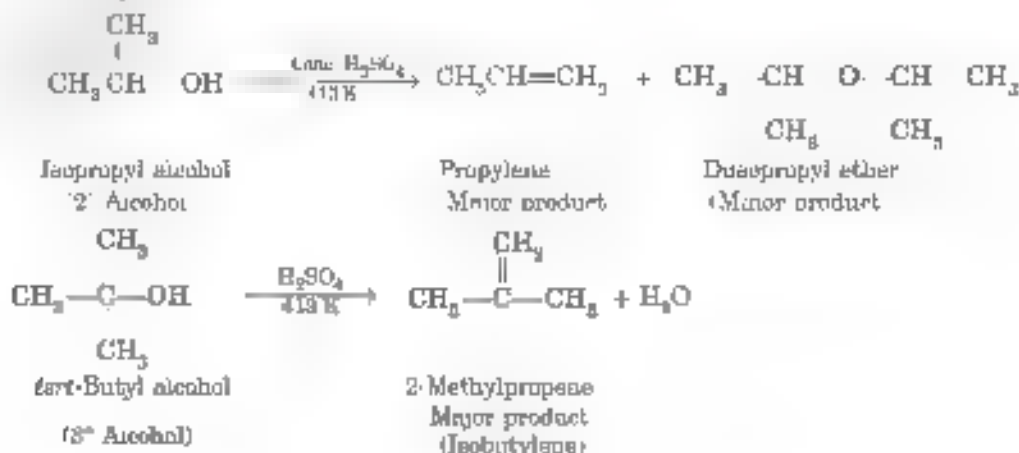
The formation of ethers may be accompanied by the formation of some amounts of alkenes. In order to avoid this, temperature of the reaction must be properly controlled because at higher temperature 443 K the alcohols get dehydrated to alkenes.



(i) A large excess of alcohols should be used.

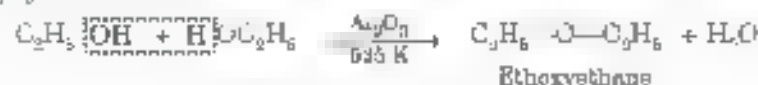
(ii) The alkyl group should be unhindered.

The above method is mainly used for the dehydration of **primary alcohols** because **secondary and tertiary alcohols** give **alkenes** as **major products** under the reaction conditions. The reaction with secondary and tertiary alcohols follows $\text{S}_{\text{N}}1$ pathway. For example,



Thus, the order of dehydration of alcohols to form ethers follows the order
primary > secondary > tertiary

The dehydration of alcohols may also be carried out by passing the vapours of alcohols over a heated catalyst like alumina (Al_2O_3) at about 525 K.



Thus, for the formation of ethers, the alkyl group should be unhindered and the temperature be kept low otherwise the reaction favours the formation of alkene.

Limitation. This method is generally not used for the preparation of unsymmetrical ethers because mixtures may be obtained. For example,

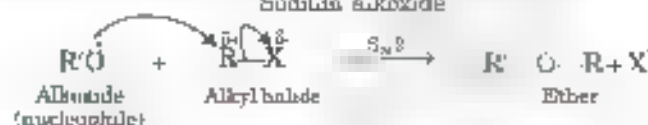


For example, ethyl methyl ether cannot be obtained by this method from methyl alcohol and ethyl alcohol



2. From alkyl halides by Williamson's synthesis

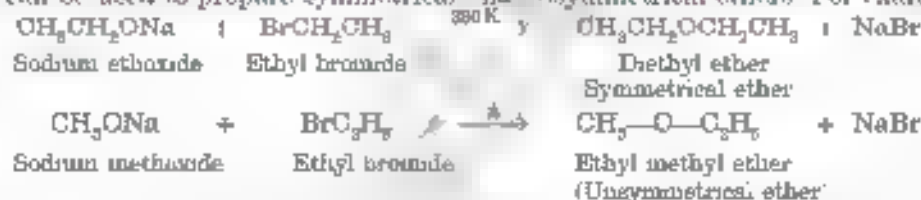
This is one of the best methods for preparing symmetrical and unsymmetrical ethers in laboratory. In this method an alkyl halide is treated with a suitable sodium alkoxide prepared by the action of sodium on a suitable alcohol. The reaction involves nucleophilic substitution ($\text{S}_\text{N}2$) attack of an alkoxide ion on primary alkyl halide.



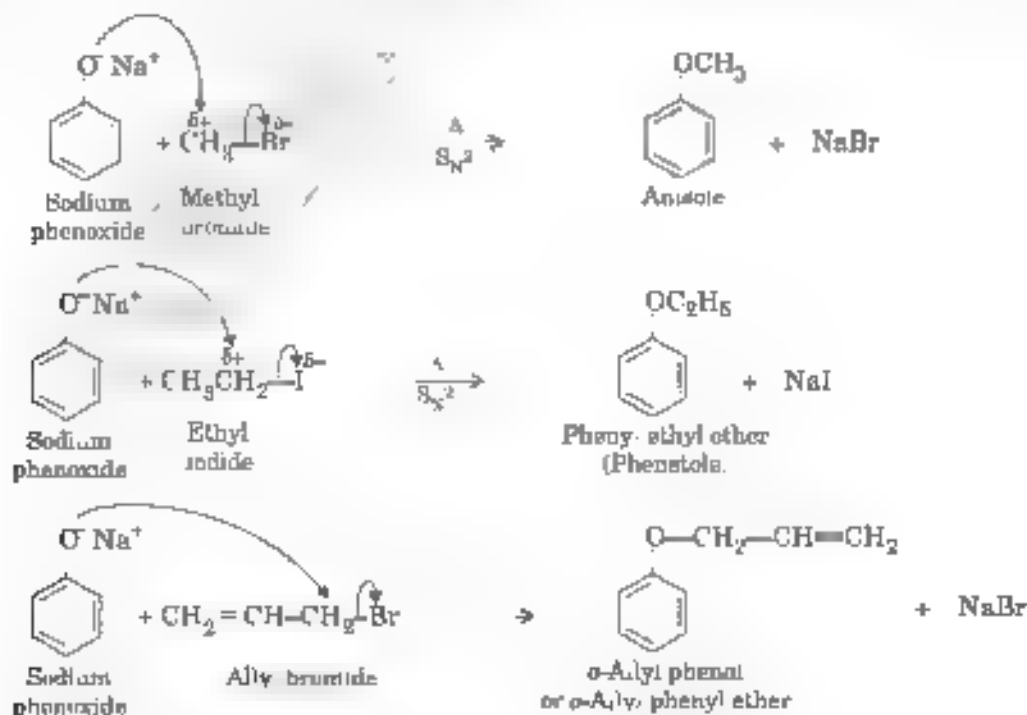
or



This reaction can be used to prepare symmetrical and unsymmetrical ethers. For example,



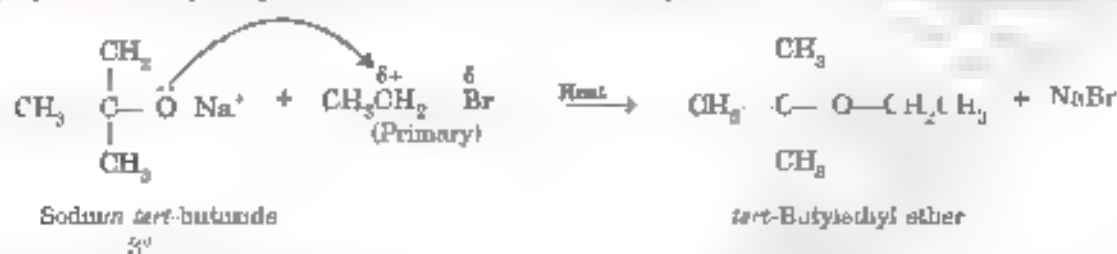
Similarly alkyl aryl ethers, phenolic ethers can be easily prepared by treating phenoxide with a suitable alkyl halide



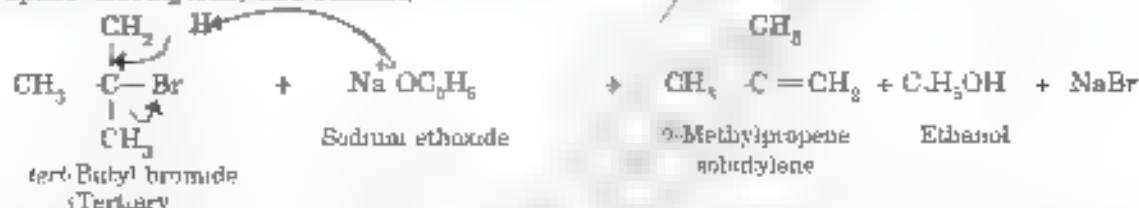
NOTE

It may be noted that phenols are more acidic than alcohols and therefore, these can be converted to sodium phenoxides by treating with NaOH . In alcohols, metallic sodium is used to convert alcohols to alkoxide ions.

Limitation. It may be noted that for preparing unsymmetrical ethers, the halide used should preferably be primary because Williamson synthesis occurs by $\text{S}_{\text{N}}2$ mechanism and primary alkyl halides are most reactive in $\text{S}_{\text{N}}2$ reactions. Therefore **best yields of unsymmetrical ethers can be obtained when alkyl halides are primary.** However the alkoxides may be primary secondary or tertiary. The secondary and tertiary alkyl halides if used may form alkenes as major product due to elimination process. For 2° and 3° alkyl halide, elimination competes over substitution. If a 3° alkyl halide is used, an alkene is the only product and no ether is formed. For example, if we want to prepare tert butyl ethyl ether then we should take ethyl bromide and sodium tert-butoxide.

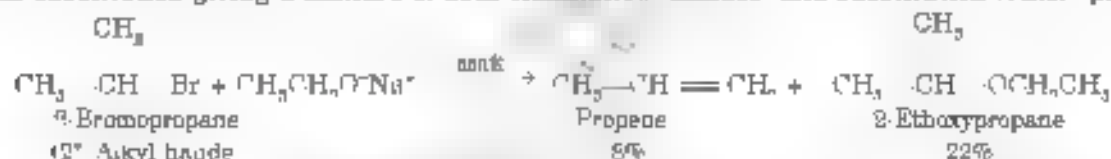


However if we use tert-butyl bromide and sodium ethoxide as reactants, then the major products would be 2-methylpropene (isobutylene) and ethanol.

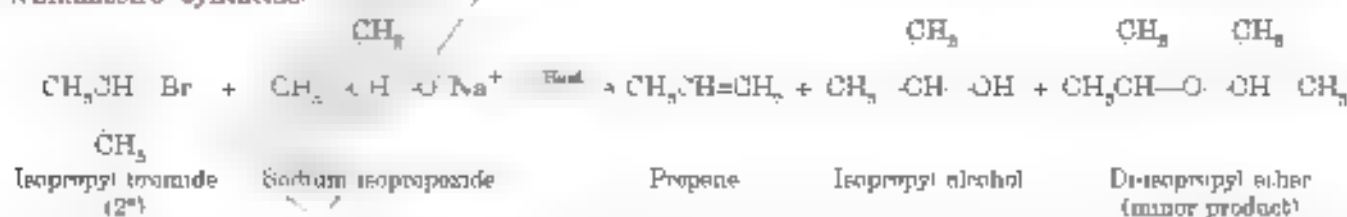


This is because alkoxides are not only nucleophiles but strong bases as well. They react with alkyl halides leading to elimination reaction.

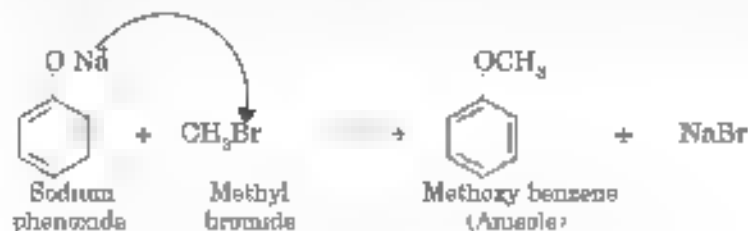
It may be noted that due to steric hindrance, secondary alkyl halides also prefer to undergo elimination rather than substitution giving a mixture of both elimination (alkenes) and substitution (ether) products. For example,



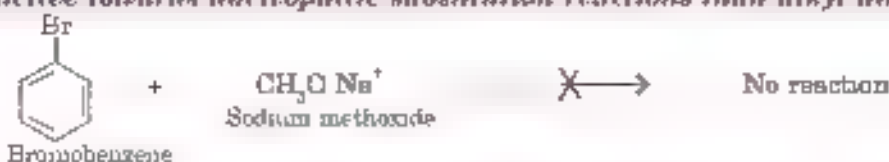
Since secondary and tertiary alkyl halides prefer to undergo elimination rather than substitution, therefore, even symmetrical ethers containing secondary and tertiary alkyl groups cannot be prepared in good yields by **Williamson's synthesis**. For example, isopropylether or di-tert-butylether cannot be prepared in good yields by Williamson's synthesis.



Further alkyl aryl ethers (phenolic ethers) can be easily prepared by using sodium phenoxide and alkyl halides. For example,



However, aryl halide and sodium alkoxide cannot be used for preparing phenolic ethers because aryl halides are less reactive towards nucleophilic substitution reactions than alkyl halides.

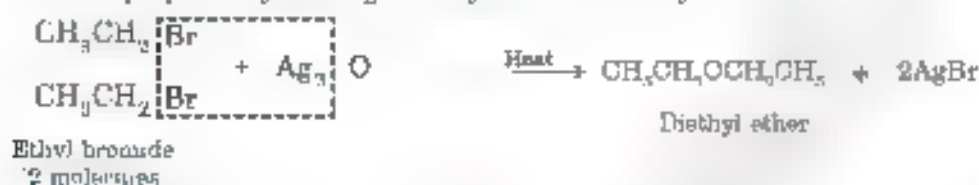


Similarly this method cannot be used for preparing dialkyl ethers because aryl halides do not undergo nucleophilic substitution reactions easily



3. From alkyl halides by treating with dry silver oxide

Ethers can also be prepared by heating an alkyl halide with dry silver oxide



4. By the action of diazomethane on alcohols

Methyl ethers can also be prepared by the action of diazomethane (CH_2N_2) on alcohols in the presence of fluoroboric acid HBF_4 as a catalyst.

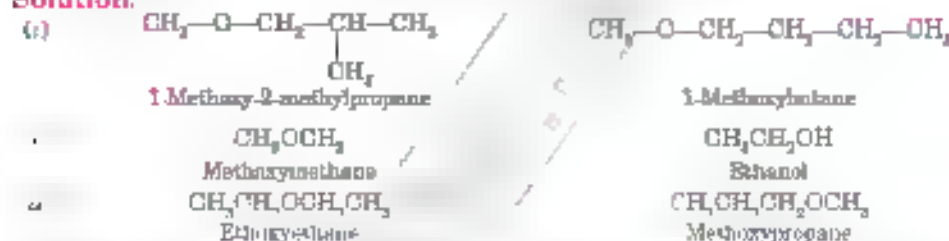


EXAMPLES

- **Example 10.**
- Write one chain isomer of 1-methoxy-3-methyl propane
 - Write one functional isomer of methoxymethane
 - Write one metamere of ethoxyethane

Pb.S.B 2006.

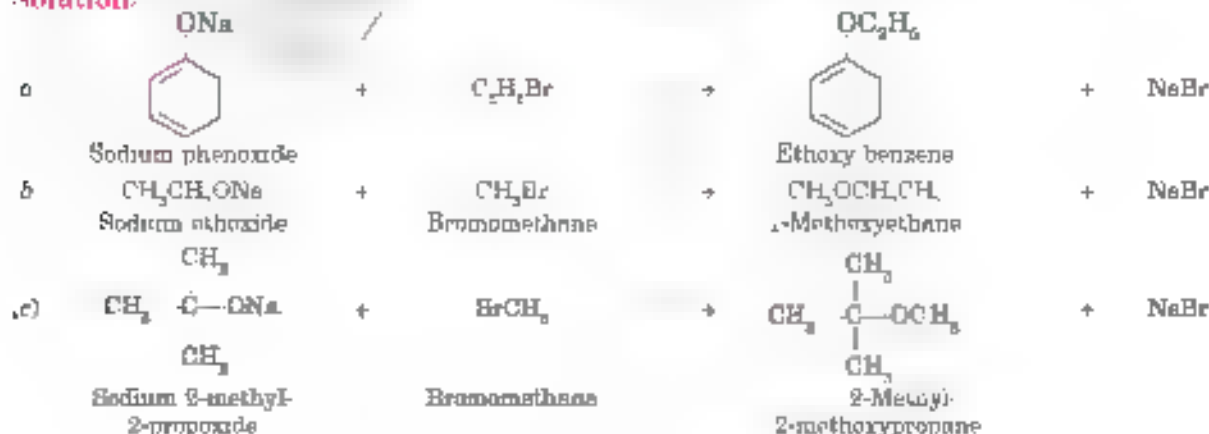
Solution.



- **Example 17** Write equations for the preparation of the following ethers by Williamson's synthesis.

- Ethoxy benzene
- 1-Methoxyethane
- 2-Methyl-2-methoxypropane
- Propoxypropane
- 1-Ethoxy-2,2-dimethylpropane

Solution:





Practice Problems

36. Suggest three methods for preparing di-*n*-propyl ether.
 37. Suggest a method to prepare ethyl-*n*-propyl ether starting from alcohol of three C-atoms or less.
 38. Name the major product in the following reactions.



- Ans. a) Ethoxy benzene $\text{C}_6\text{H}_5\text{OC}_2\text{H}_5$ b) Ethyl methyl ether $\text{C}_2\text{H}_5\text{OCH}_3$
 (c) Isobutylene $(\text{CH}_3)_2\text{C}=\text{CH}_2$ (d) Tert-butyl ethyl ether

PHYSICAL PROPERTIES OF ETHERS

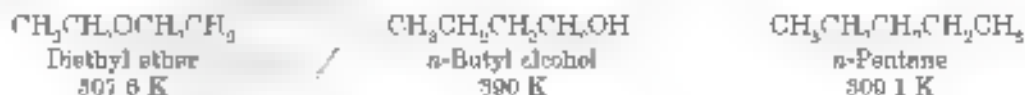
The important physical properties of ethers are

1. Physical state. Lower members dimethyl ether, methyl ethyl ether are gases and higher members are low boiling liquids with a pleasant smell.

2. Dipole moments. Ethers have bent or angular structure like water. Due to greater electronegativity of oxygen than carbon, the C-O bonds are slightly polar and therefore the ethers have resultant dipole moment. Since the two C-O bonds are inclined to each other at an angle of about 110° , two dipoles do not cancel each other. As a result, ethers have resultant dipole moment. For example, dipole moment of dimethylether is 1.3D and that of diethylether is 1.15D.



3. Boiling points. Ethers have low polarity and as a result do not show any association by intermolecular hydrogen bonding. Therefore, ethers have low boiling points and lower than that of isomeric alcohols and almost same as those of alkanes of comparable molecular masses.



The large difference in boiling points of alcohols and ethers is due to the presence of hydrogen bonding in alcohols.

The boiling points of ethers increase with increase in number of carbon atoms. Due to weak dipole-dipole forces, the boiling points of lower members such as dimethyl ether and ethyl methyl ether are only slightly higher than those of the corresponding *n*-alkanes of comparable molecular masses. The boiling point of diethyl ether is almost the same (307.6 K) as that of *n*-pentane (309.1 K) having comparable molecular masses. However, as the hydrocarbon part increases beyond four carbon atoms, the boiling points of ethers are even slightly lower than corresponding *n*-alkanes of comparable molecular masses. This is because of the presence of oxygen atom, ether molecules are less symmetrical than *n*-alkanes of comparable molecular masses. Therefore, the van der Waals forces of attraction between ether molecules are slightly less than those in the more symmetrical *n*-alkanes of comparable molecular masses. For example,

Ether	CH_3OCH_3	$\text{CH}_3\text{OC}_2\text{H}_5$	$\text{C}_2\text{H}_5\text{OC}_2\text{H}_5$	$\text{C}_2\text{H}_5\text{OC}_3\text{H}_7$	$\text{C}_2\text{H}_5\text{OC}_4\text{H}_9$
Molecular mass	46	60	74	88	102
Boiling point (K)	250	283	307.6	306.0	300



This reaction can be used to distinguish between ethers and alkanes because alkanes do not react with dilute acids.

3. **Reaction with Lewis acids (formation of coordination complexes).** Being Lewis bases, ethers form coordination complexes with Lewis acids such as BF_3 , AlCl_3 , FeCl_3 , etc. These complexes are called **etherates**.



Similarly, diethyl ether reacts with Grignard reagent, forming Grignard reagent etherate.

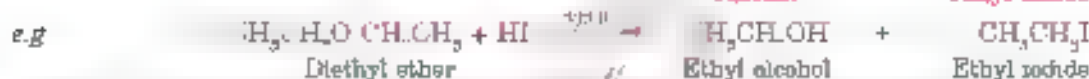
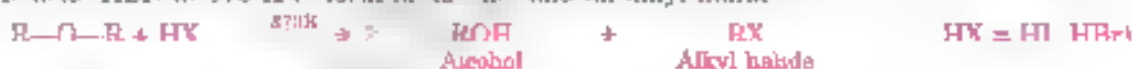


Due to the formation of the etherate, Grignard reagents dissolve in ether. That is why Grignard reagents are usually prepared in ethers. However, they cannot be prepared in benzene, because benzene has no lone pair of electrons and therefore, cannot form complexes with them.

B. Reactions Involving Cleavage of C—O Bond

Ethers are the least reactive of the functional groups. Carbon-oxygen bond in ethers can be cleaved under drastic conditions as given below.

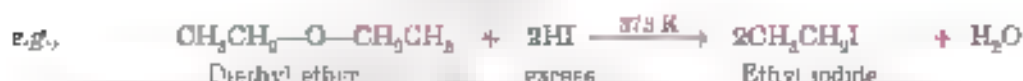
1. **Cleavage by halogen acids.** The carbon-oxygen bond in ethers can be cleaved by heating with hydroiodic acid and HI and hydrobromic acid HBr, at 373 K to form an alcohol and an alkyl halide.



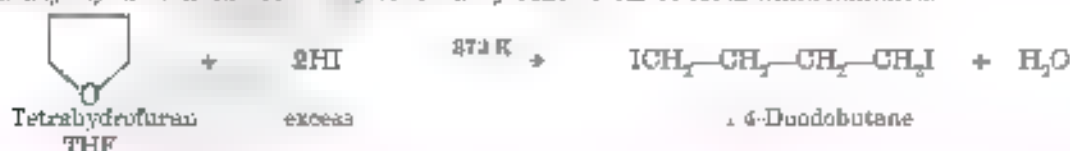
However, if excess acid is used, the alcohol first formed reacts further with the halogen acid to form alkyl halide.



The overall reaction may be written as



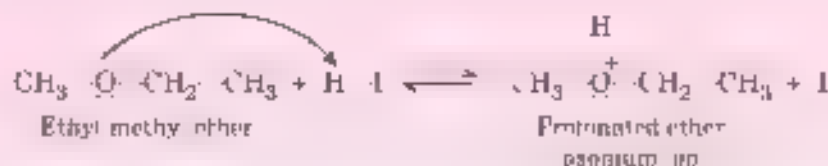
Similarly, cyclic ethers are easily cleaved by HBr or HI to form dialkylalkanes.



Reaction 10: Cleavage of C—O bond in ethers by halogen acids

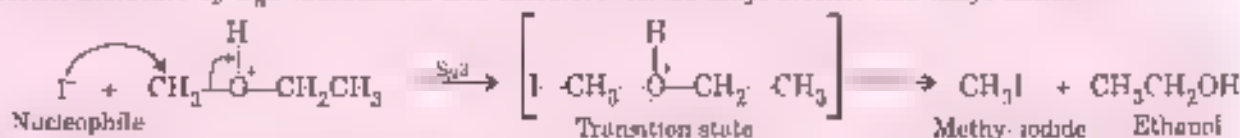
The cleavage reaction follows the following mechanism:

1. The ether molecule being Lewis base gets protonated by the hydrogen of the acid to form protonated ether or oxonium salt.

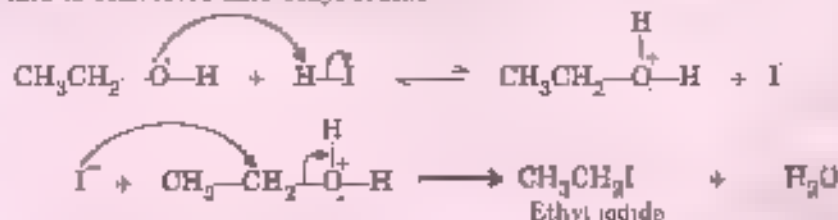


The reaction takes place with HBr and HI because these reagents are sufficiently acidic.

2. Iodide ion, I^- , is a good nucleophile. The protonated ether undergoes nucleophilic attack by iodide ion, I^- , and displaces an alcohol molecule by S_N2 mechanism and therefore forms alkyl iodide and alkyl halide.



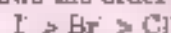
3. When HI is in excess and the reaction is carried out at high temperature, ethanol formed reacts with another molecule of HI and is converted into ethyl iodide.



The order of reactivity of halogen acids is

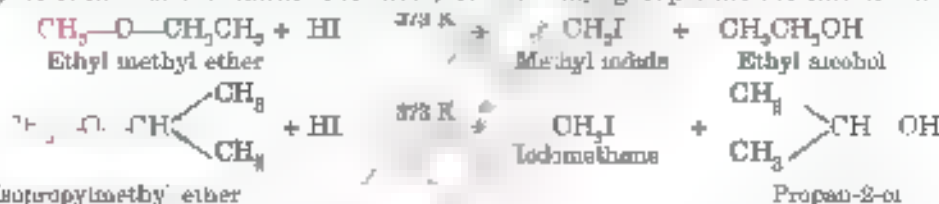


As we have seen above, the cleavage of ethers by halogen acids involves nucleophilic attack by halide ion, X^- , on the protonated ether. Therefore, greater the nucleophilicity of the halide ion, more reactive is the halogen acid. As we know, nucleophilicity of the halide ions follows the order

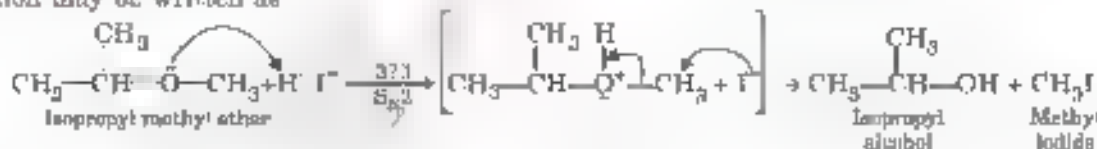


Therefore, the reactivity of the halogen acids follows the same sequence, i.e., $HI > HBr > HCl$.

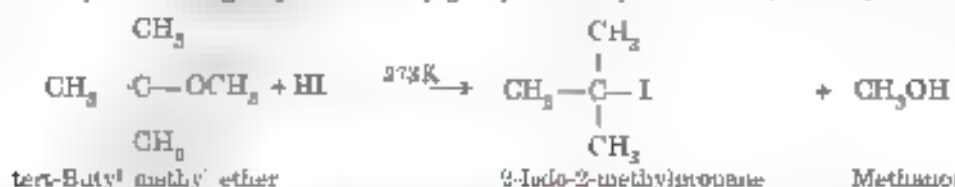
● **Cleavage of unsymmetrical alkyl ethers (site of cleavage)** In case of unsymmetrical ethers having two different alkyl groups, the alcohol and the alkyl iodide formed depend upon the nature of the alkyl groups. If primary and secondary alkyl groups are present then the reaction occurs by **S_N2 mechanism**. The halide ion attacks the smaller alkyl group because of less steric hindrance. Thus, in case of unsymmetrical ethers with two different alkyl groups, the site of cleavage is such that the halide is formed from the alkyl group which is smaller in size. For example,



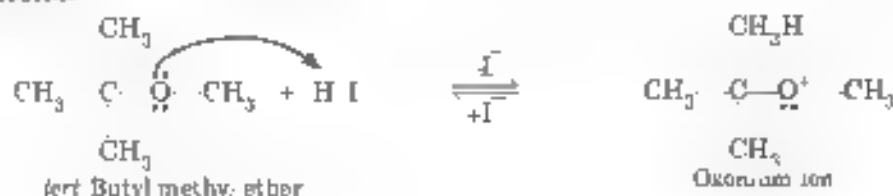
The reaction may be written as

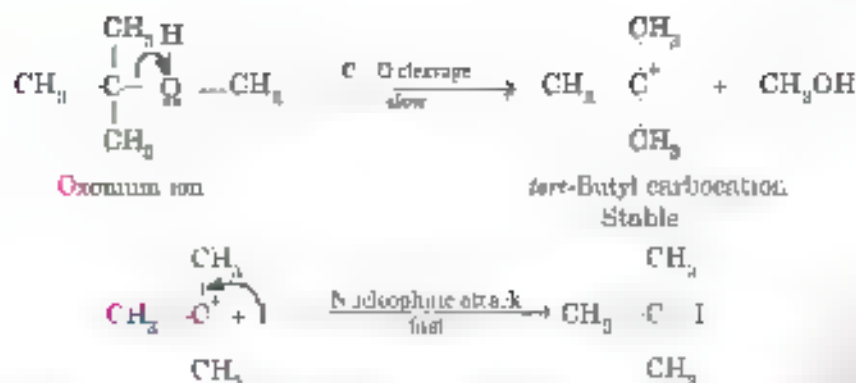


If, however, one of the alkyl groups is tertiary group, the alkyl iodide is formed from the tertiary alkyl group.

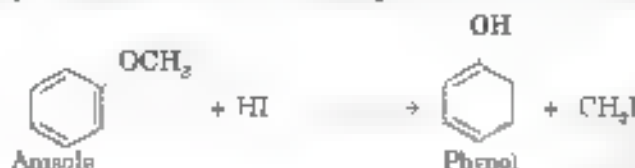


This is because the reaction now occurs by **S_N1 mechanism**. The formation of products is governed by the stability of the carbocation formed from the cleavage of $\text{C}-\text{O}$ bond in the protonated ether (oxonium ion). Since *tert*-butyl carbocation, $(\text{CH}_3)_3\text{C}^+$, is more stable than the methyl carbocation, CH_3^+ , therefore, cleavage of $\text{C}-\text{O}$ bond gives a more stable carbocation, $(\text{CH}_3)_3\text{C}^+$, and methanol. Then, iodide ion, I^- , attacks this *tert*-butyl carbocation to form *tert*-butyl iodide.





● **Cleavage of alkyl aryl (phenolic) ether** With alkyl aryl ethers phenols rather than alcohols are formed. The cleavage in a hydrogen halide always gives phenol and a molecule of alkyl halide and not aryl halide and alcohol.



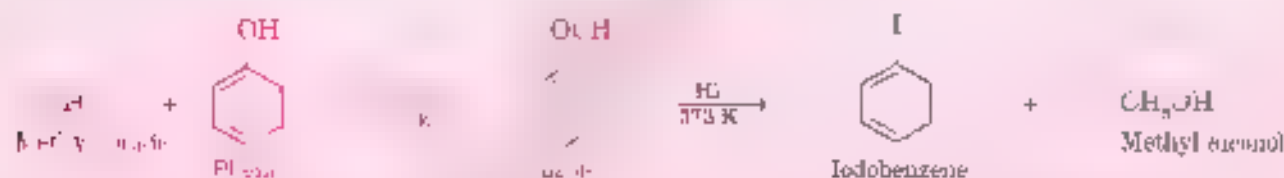
NOTE

Unlike alkyl alcohols phenol does not react further with HI to give aryl halide because of strong carbon-oxygen bond in phenol.

In case of anisole, methylphenyl oxonium ion, $\text{C}_6\text{H}_5 - \overset{+}{\text{O}} - \text{CH}_3$ is formed by the protonation of ether. The bond

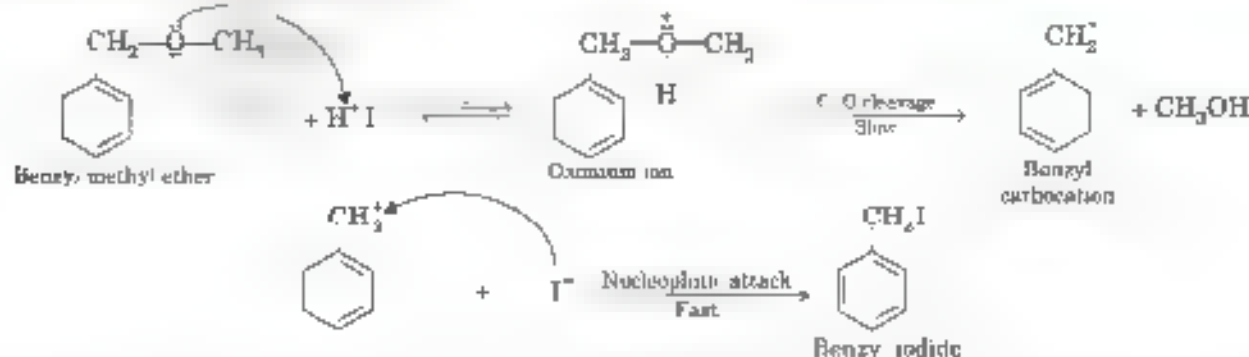
between $\text{O}-\text{CH}_3$ is weaker than the bond between $\text{C}-\text{C}_6\text{H}_5$ bond as the carbon of phenyl group is sp^2 hybridised and there is partial double bond character. Therefore, the attack of halide ion breaks $\text{C}-\text{O}-\text{CH}_3$ bond to form CH_3X . It may be noted that phenols do not react further to give aryl halides because the sp^2 hybridised carbon of phenol does not undergo nucleophilic substitution reaction. This can also be explained on the basis of steric hindrance. The alkyl halide is formed by the attack of halide ion on the protonated ether. Therefore, the attack of nucleophile occurs on smaller alkyl group which offers less hindrance.

Therefore, alkyl halide is formed from smaller alkyl group. Thus,



NOT FORMED

● **Cleavage of benzyl alkyl ethers.** In case of benzyl alkyl ethers containing a primary alkyl group such as benzyl methyl ether, the reaction proceeds by $\text{S}_{\text{N}}1$ mechanism. Since the benzyl carbocation is more stable than the methyl carbocation, the cleavage of $\text{C}-\text{O}$ bond gives benzyl carbocation and methyl alcohol. The halide ion then attacks carbocation to form benzyl iodide.

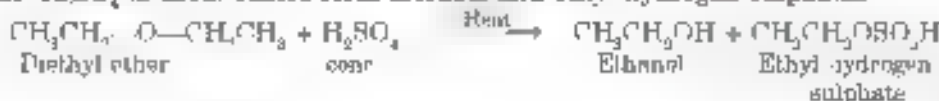


● **Cleavage of diaryl ethers.** It may be noted that diaryl ethers such as diphenyl ether are not cleaved by HI. This is because the $\text{C}-\text{O}$ bonds have some double bond character due to resonance between the lone pairs of electrons on the O atom and the C atoms of aryl groups (benzene ring) directly bonded to the O atom.

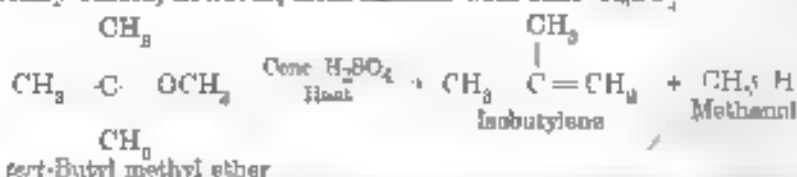
2. **Cleavage by sulphuric acid.** On heating with $\text{dil. H}_2\text{SO}_4$ under pressure, ethers are hydrolysed to give alcohols.



If conc. H_2SO_4 is used, ethers form alcohols and ethyl hydrogen sulphates



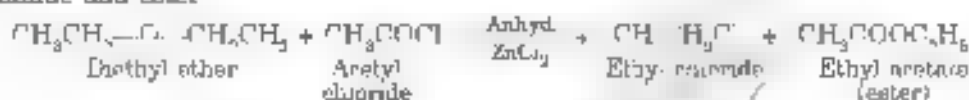
Secondary and tertiary ethers, however, form alkenes with conc H_2SO_4 .



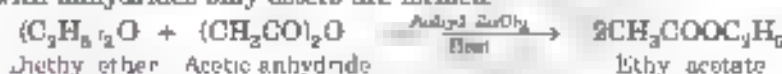
3. Cleavage with phosphorus pentachloride. Ethers react with PCl_5 on heating to form alkyl chloride as a result of cleavage of C—O bond.



4. Cleavage by acid chlorides. Ethers react with acetyl chloride in the presence of anhydrous ZnCl_2 to give alkyl halide and ester.



However, with anhydrides only esters are formed.

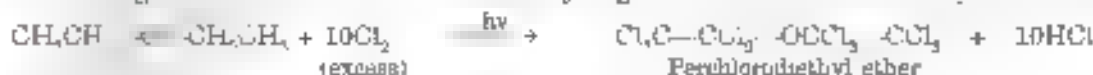


↪ Reactions of Alkyl Group

1. Halogenation. Ethers react with chlorine or bromine in the dark to give substituted products. The extent of substitution depends upon the reaction conditions. For example, diethyl ether reacts with chlorine in the dark to give 1,1-dichlorodiethyl ether in which the halogenation preferentially occurs at α -carbon atoms.



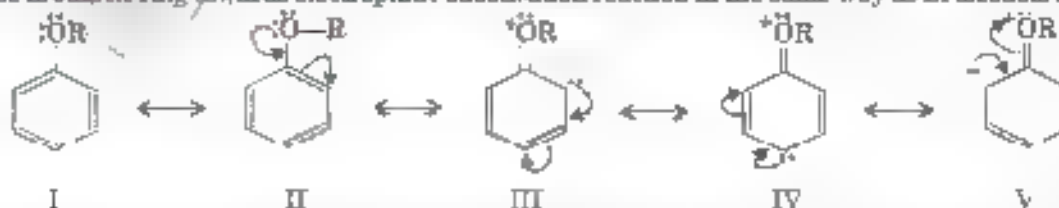
However, in the presence of light and excess of chlorine all the hydrogen atoms are substituted by chlorine atoms.



D. Ring Substitution in Aromatic Ethers

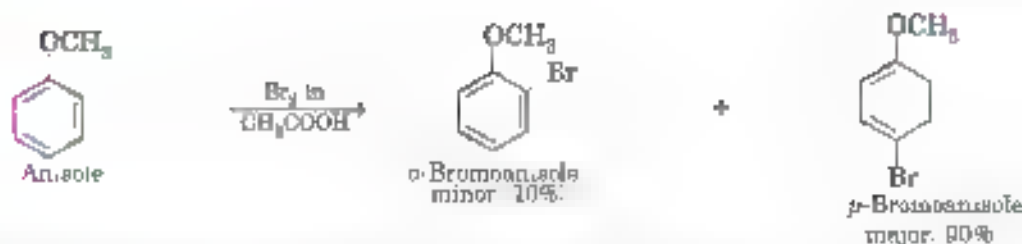
Alkoxy group is **ortho and para directing** and it directs the incoming groups to **ortho** and **para** positions.

It activates the aromatic ring towards electrophilic substitution reaction in the same way as in alcohols as given below



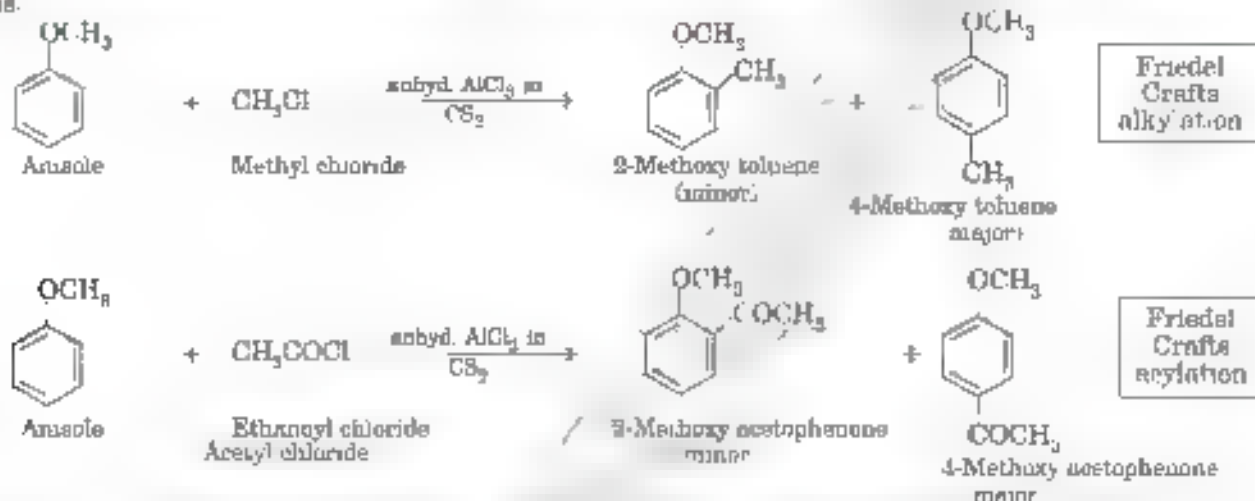
As is clear that structures III, IV and V show high electron density at *ortho* and *para* positions as compared to *meta* position. Therefore, electrophilic substitution reactions occur mainly at *o*- and *p*- positions.

1. **Halogenation.** Phenyl alkyl ethers undergo usual halogenation in the benzene ring. For example, bromination of anisole gives *ortho* and *para* bromo derivatives even in the absence of iron (III) bromide catalyst. It is due to the activation of benzene ring by methoxy group.

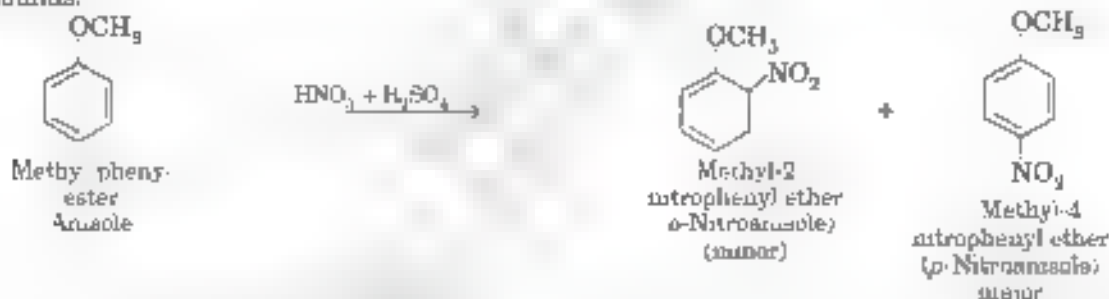


Para isomer is obtained in 90% yield.

2. Friedel Crafts reaction. Anisole undergoes **Friedel-Craft alkylation** and acylation reactions in the presence of anhydrous aluminum chloride as a Lewis acid catalyst in which alkyl and acyl groups are introduced at *ortho* and *para* positions.



3. Nitration. When treated with a mixture of concentrated HNO_3 and H_2SO_4 , anisole gives a mixture of *o*- and *p*-nitro compounds.

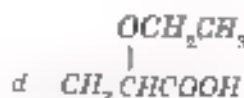
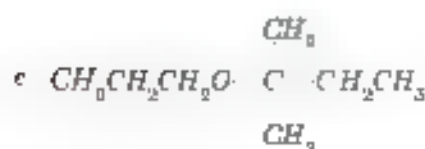
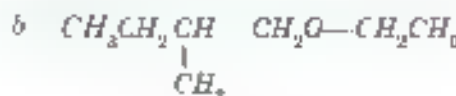
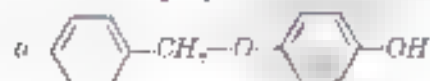


It may, however, be noted that ethers are relatively **less reactive** than phenols towards electrophilic substitution reactions.

SOLVED EXAMPLES

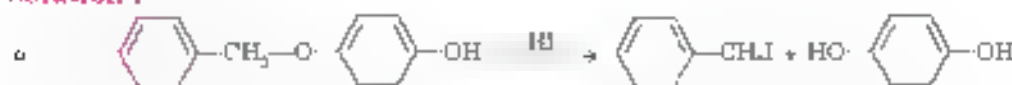
Example 18.

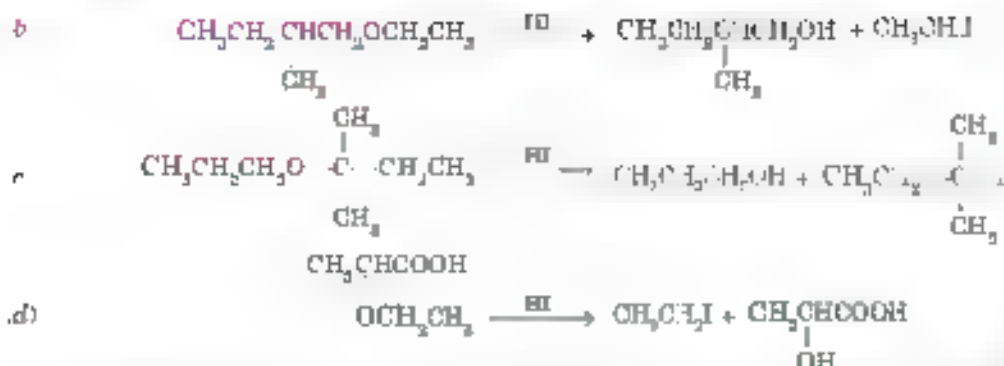
Give the major products that are formed by heating each of the following ethers with HI



[N.C.E.R.T.]

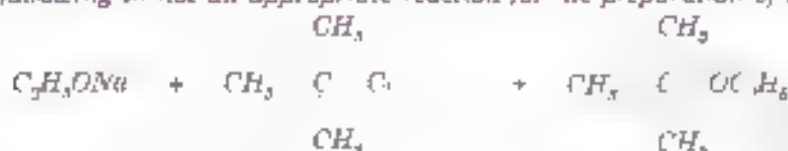
Solution .





Example 10.

The following is not an appropriate reaction for the preparation of *tert*-butyl ether

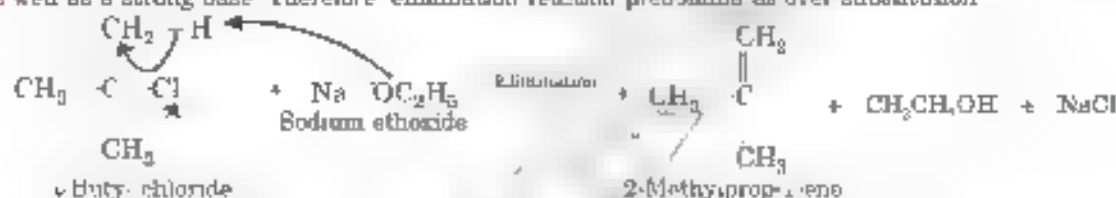


(a) What would be the major product of the reaction?

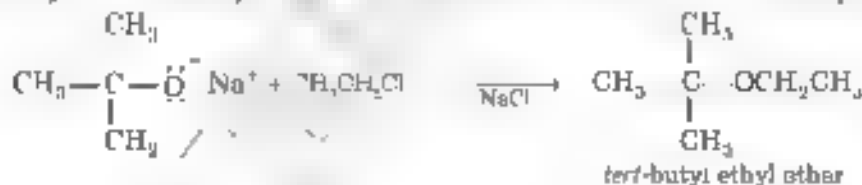
(b) Write a suitable reaction for the preparation of *tert*-butyl ethyl ether

[N.C.E.R.T.]

Solution : The major product of the given reaction is 2-methylprop-1-ene. This is because sodium ethoxide is a strong nucleophile as well as a strong base. Therefore, elimination reaction predominates over substitution.



To prepare *tert*-butyl ethyl ether, the alkyl halide should be 1-chloroethane and the nucleophile should be sodium *tert*-butoxide.

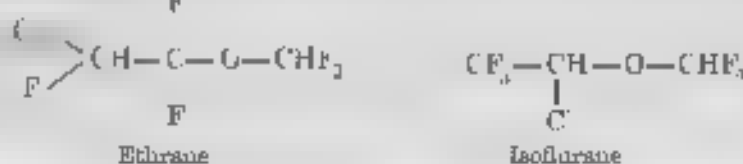


USES OF ETHERS

Ethers are widely used as solvents both in laboratory as well as in industry because of their almost inert nature and good dissolving power. Among these, methyl ether is very common. The important uses of diethyl ether are

1. Diethyl ether is an industrial solvent for oils, fats, gums, resins, etc.
2. It is used in surgery as an anaesthetic.

Ethoxy ethane is widely used as an inhalation anaesthetic. However, because of its slow effect and unpleasant recovery period, ethoxy ethane has been replaced by other compounds such as ethrane and isoflurane as anaesthetics.



3. It is also used as a refrigerant.
4. It is also used as a reaction medium in LiAlH_4 reductions and Grignard synthesis.
5. It is used as an extracting solvent in laboratory and industry.
6. When mixed with alcohol it acts as a denaturant and the mixture is used as petrol substitute under the trade name *Natohite*.
7. It is used in perfumery and in the manufacture of smokeless powder.

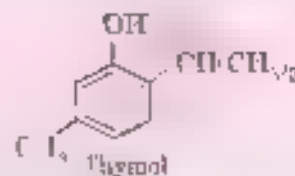
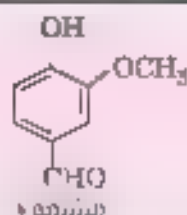
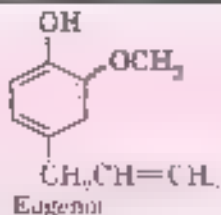
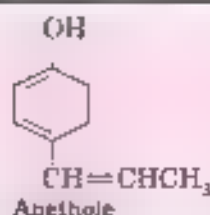
Dimethyl ether is used in the form of compressed liquid as a refrigerant, low temperature solvent and propellant for sprays. It is also used for storing food stuffs by freezing in direct contact because it does not leave any undesirable taste or smell.

Di isopropyl ether is used as an industrial solvent and for reducing knocking of petrol.

Divinyl ether is used as an anaesthetic and is considered better than diethyl ether because of its rapid action and rapid recovery from anaesthesia.

Phenyl ether has been used as heat transfer medium because of its high boiling point (631 K).

A number of naturally occurring phenols and ethers, particularly ring substituted anisoles are used as flavouring and in perfumes because of their pleasant odour. For example, **anethole** is constituent of anise seed, **eugenol** present in oil of cloves, **vanillin** present in oil of vanilla bean and **thymol** present in thyme and mint are some common examples of phenols and ethers used in perfumes and flavourings.



add on

Conceptual Questions 2

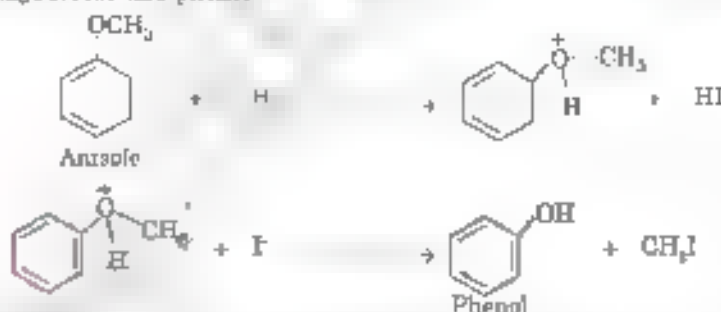
Q. 1. Write the structure of phenyl isopentylether.

(CBSE Sample Paper 2011)

Ans. $\text{C}_6\text{H}_5\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}(\text{CH}_3)_2$

Q. 2. Anisole on reaction with HI gives phenol and CH_3I as main products and not iodobenzene and CH_3OH . (A.I.S.B. 2010)

Ans. If the reaction protonated anisole i.e. methylphenyl oxonium ion is first formed and then the halide ion attacks the protonated anisole. Due to steric hindrance of bulky phenyl group, the attack preferably occurs on the alkyl group forming methyl iodide and phenol.



Q. 3. Why are ethers relatively inert compounds?

Ans. Ethers are inert compounds because the functional group of ethers $-\text{O}-$ does not contain any active site. Therefore, under ordinary conditions, they are stable to bases, dilute acids and other oxidising and reducing agents.

Q. 4. Why di-*tert*-butyl ether cannot be prepared by Williamson synthesis?

Ans. To prepare di-*tert*-butyl ether by Williamson's synthesis, we require *tert*-butyl bromide and sodium *tert*-butoxide. Since *tert*-butyl bromide is a 3° alkyl halide, it prefers to undergo elimination rather than substitution. Therefore, isobutylene is obtained as the product rather than di-*tert*-butyl ether.



Q. 5. Name the pair of alkyl halide and alkoxide for the preparation of ethyl *tert*-butyl ether.

Ans. Ethyl iodide and sodium *tert*-butoxide

Q. 6. What products are obtained when



Key Terms & Name Reactions

- **Esterification.** The reaction of alcohols and carboxylic acids in the presence of conc. H_2SO_4 to form esters
- **Hydrogenolysis.** Catalytic hydrogenation is called hydrogenolysis
- **Hydroboration oxidation reduction.**



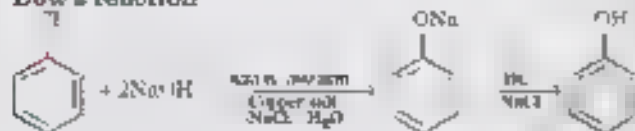
e.g. $CH_3CH=CH_2 \xrightarrow[\text{in } H_2O_2, OH^-]{\Delta, H_2B, THF} CH_3-CH_2-CH_2OH$ according to Anti-Markovnikov's rule

- **Oxymercuration-demercuration reaction**

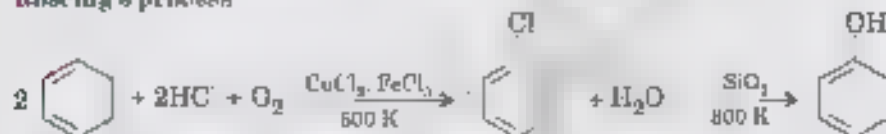


e.g. $CH_3CH_2CH=CH_2 \xrightarrow[\text{in } NaOH]{\Delta, Hg(OAc)_2, THF} CH_3CH_2-\overset{\text{H}}{\underset{OH}{\text{C}}}-CH_3$ according to Markovnikov's rule

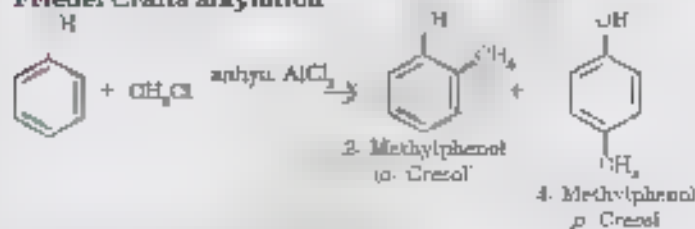
- **Dow's reaction**



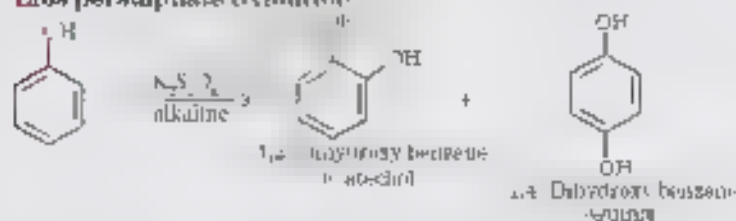
- **Raschig's process**



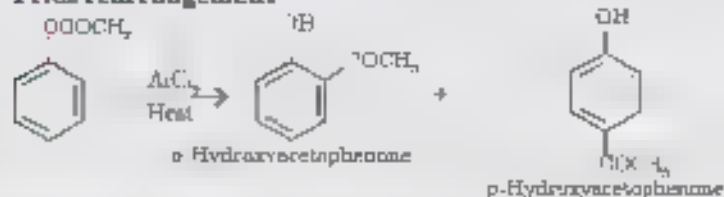
- **Friedel Crafts alkylation**



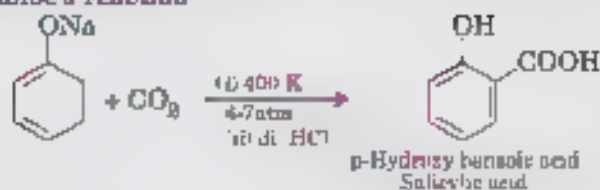
- **Ellis persulphate oxidation**



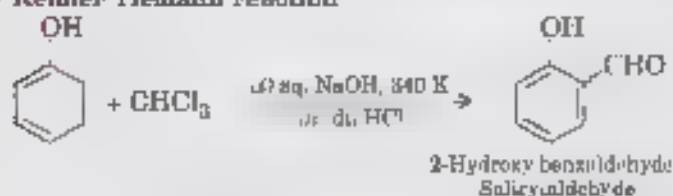
- **Fries rearrangement**



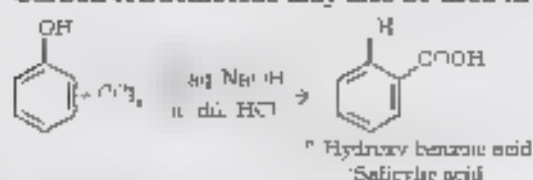
- **Kolbe's reaction**



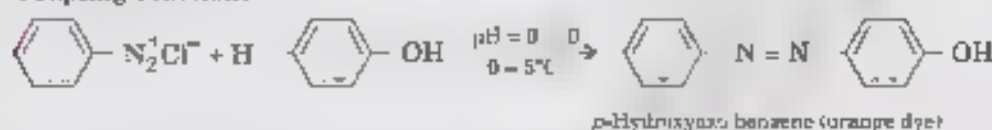
- **Reimer Tiemann reaction**



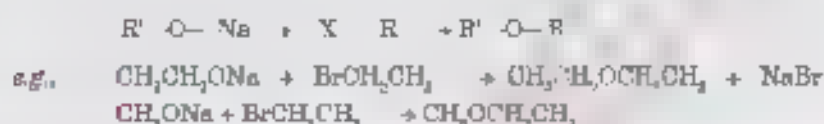
Carbon tetrachloride may also be used in place of chloroform.



- **Coupling reactions**



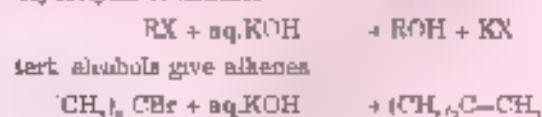
- **Williamson's synthesis**



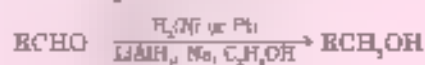
QUICK CHAPTER ROUND UP

Preparation of Alcohols

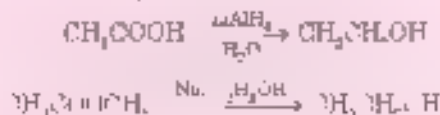
- **Hydrolysis of alkanes**



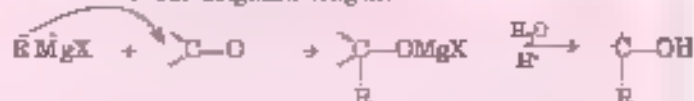
- **Reduction of aldehydes/ketones**



- **Reduction of carboxylic acids/esters**



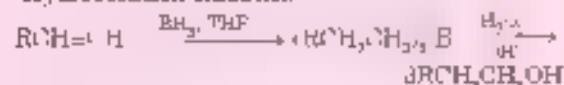
- **From Grignard reagent**



- **From alkenes hydrolysis**

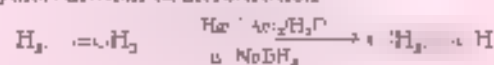


- **Hydroboration-oxidation**



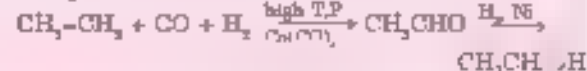
anti-Markovnikov rule

- **Oxymercuration-demercuration**



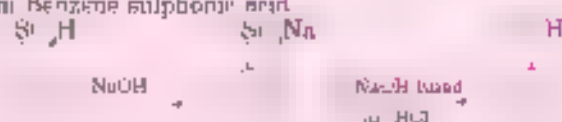
Markovnikov's addition reaction

- **Oxo process**



Preparation of Phenols

- From Benzene sulphonyl acid



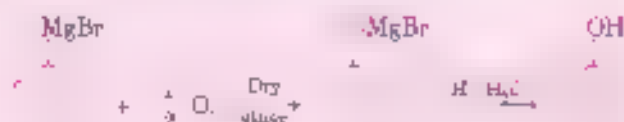
- From diazonium salt



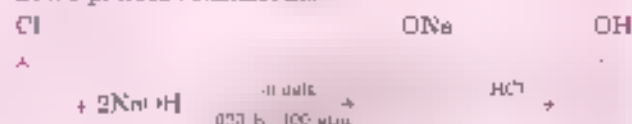
- By decarboxylation



- From Grignard reagent



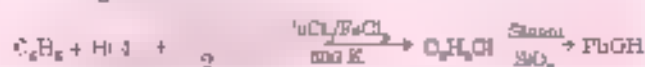
- Dow's process (Commercial)



- From Cumene



- Rainberg's method

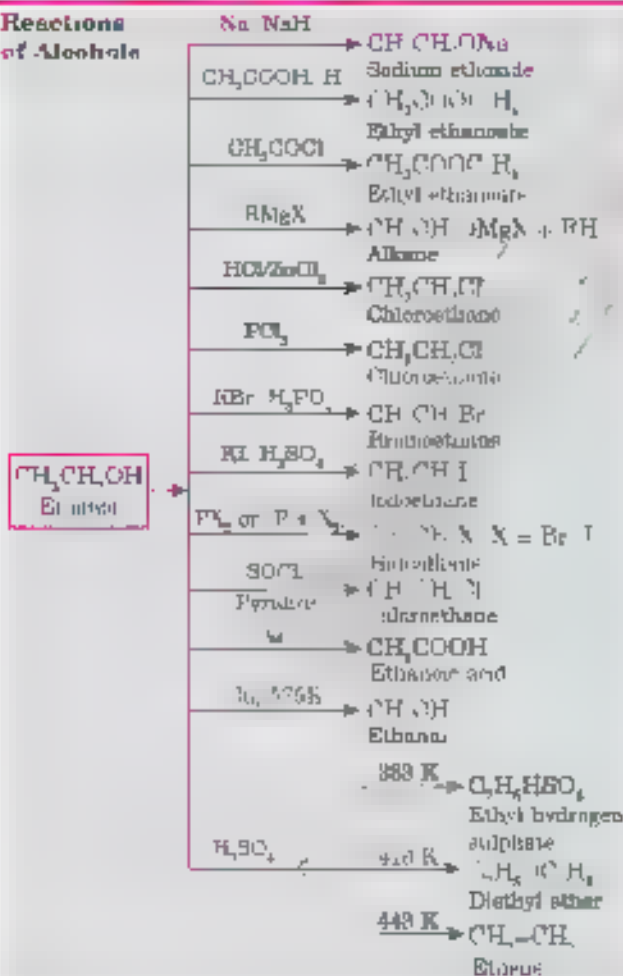


Alcohols are weaker acids than water

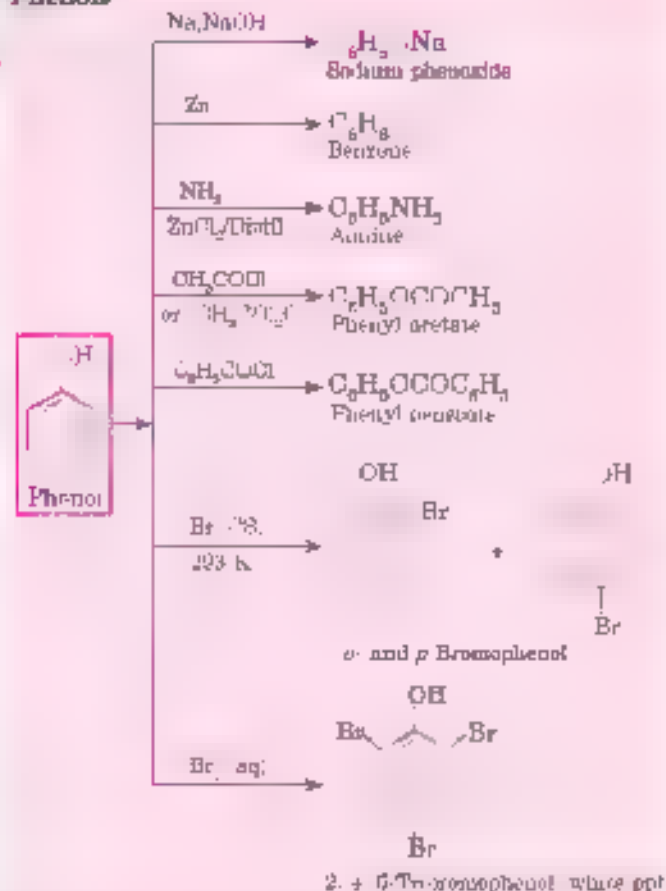
Phenol is more acidic than ethyl alcohol

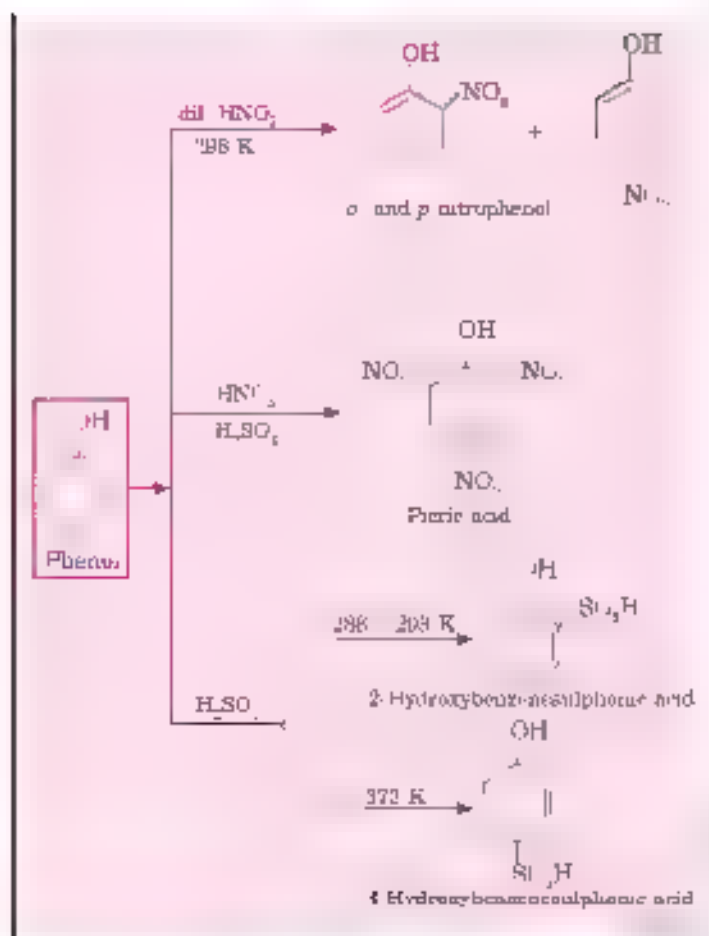
- Electron withdrawing groups (NO_2 , CN , X) increase acidic strength
- Electron donating groups ($-\text{R}$, $-\text{NH}_2$, $-\text{OR}$) decrease acidic strength.

Reactions of Alcohols

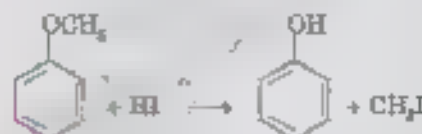
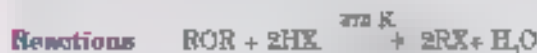
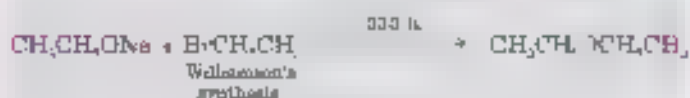
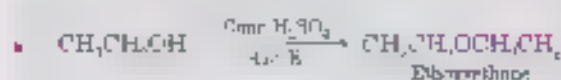


Reactions of Phenols



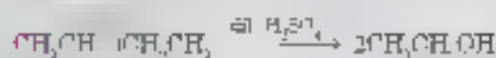


Ethers are called **alkoxy alkanes**.



• In alkyl aryl ethers, the products are always phenol and alkyl halide and never an aryl halide and alcohol.

• Diaryl ethers such as diphenyl ethers are not cleaved by HI.



Alkoxy group is *o*- and *p*-directing group in electrophilic substitution reactions.



NCERT FILE

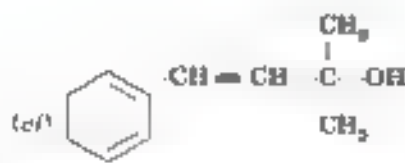
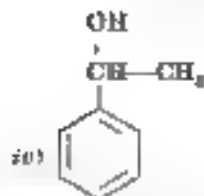
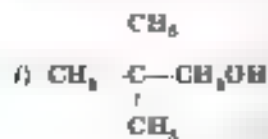
Solved



NCERT

In-text Questions

Q.1 Classify the following as primary, secondary and tertiary alcohols :

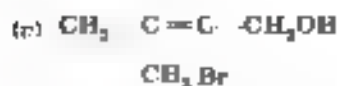
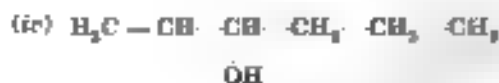
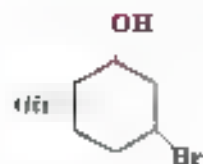
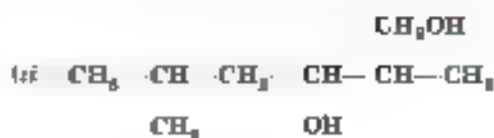
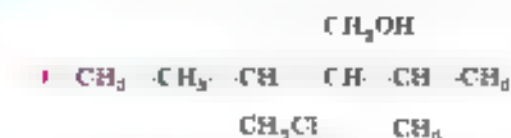


Ans. i) Primary alcohol ii) Primary alcohol iii) Primary alcohol iv) Secondary alcohol v) Secondary alcohol vi) Tertiary alcohol

Q.2 Identify allylic alcohols in the above examples.

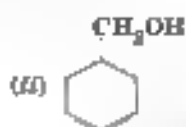
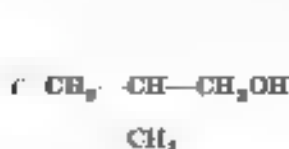
Ans. ii) and vi) are allylic alcohols.

Q.3. Name the following compounds according to IUPAC system

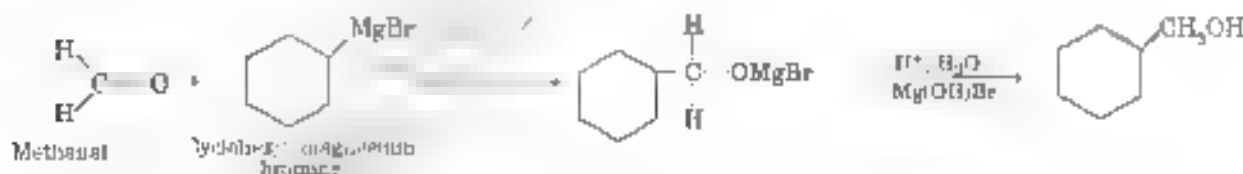
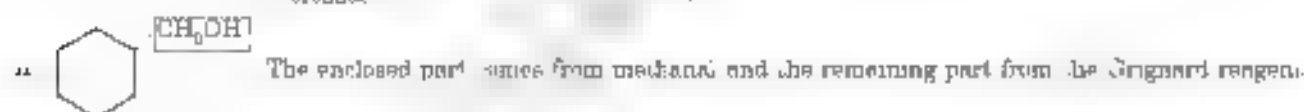
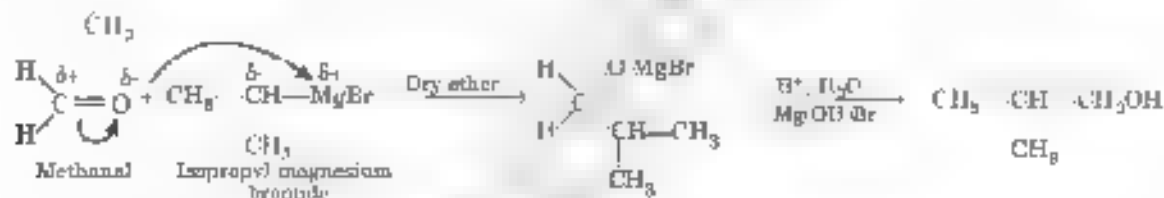


Ans. Refer Solved Example 2 page 8.

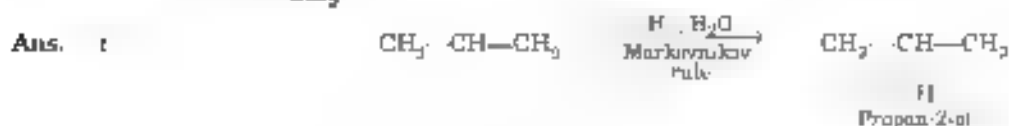
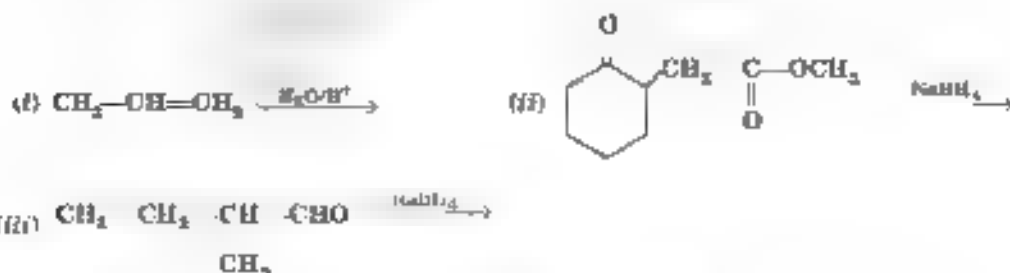
Q.4. Show how are the following alcohols prepared by the reaction of a suitable Grignard reagent on methanal?

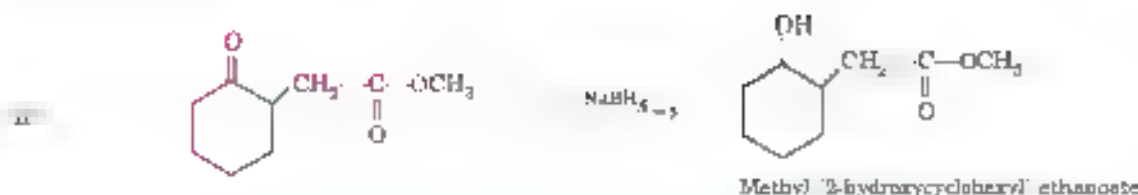


Ans. (i) $\text{CH}_3 - \text{CH} - \text{CH}_2\text{OH}$. The enclosed part comes from methanal and the remaining part comes from the Grignard reagent.



Q.5. Write structures of the products of the following reactions:



**HELP**

NaBH_4 is a weak reducing agent and reduces the aldehydes and ketones and not the esters

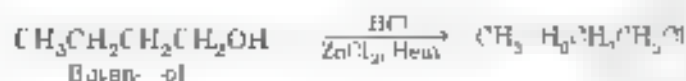


Q.6. Give structures of the products you would expect when each of the following alcohol reacts with
 (a) $\text{HCl}-\text{ZnCl}_2$, (b) HBr and (c) SOCl_2 .

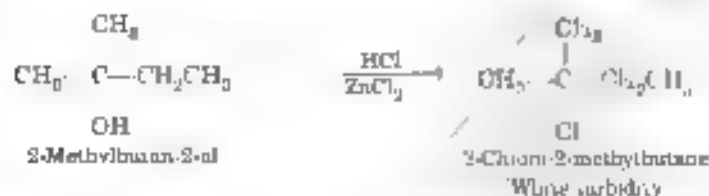
i Butan-1-ol

ii 2-Methylbutan-2-ol

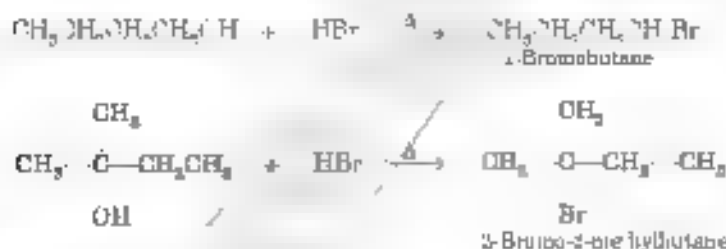
Ans. *a* $\text{HCl}-\text{ZnCl}_2$. It is Lucas reagent. Butan-1-ol does not react with $\text{HCl}-\text{ZnCl}_2$ at room temperature. However turbidity appears only upon heating.



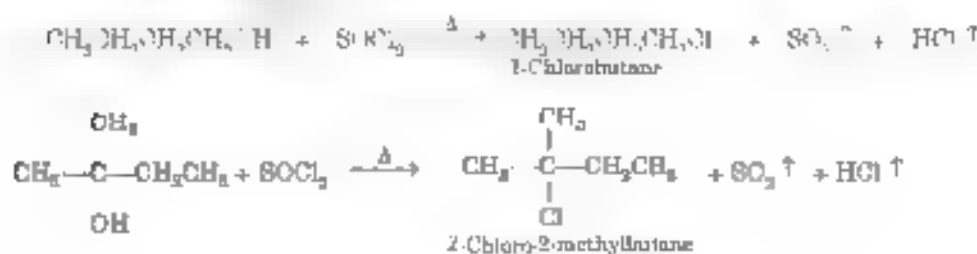
But 2-methylbutan-2-ol *ii* reacts at room temperature giving turbidity immediately.



b HBr . Both alcohols react with HBr to give corresponding alkyl bromides.

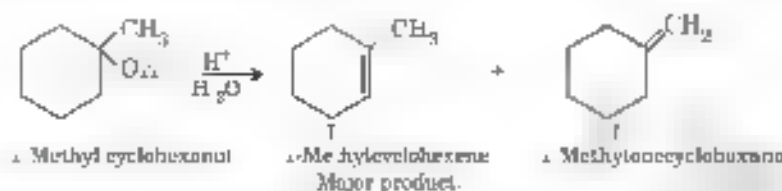


c SOCl_2 . Both alcohols react to give corresponding alkyl chlorides.

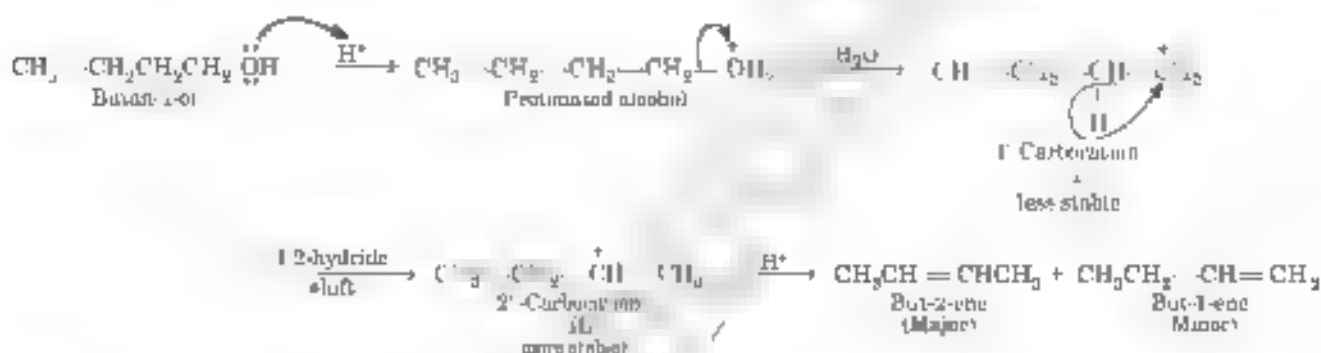


Q.7 Predict the major product of acid catalysed dehydration of (i) 1-methyl cyclohexanol and (ii) butan-1-ol

Ans. Acid catalysed dehydration of 1-methylcyclohexanol gives two products I and II. But product I is highly substituted and hence, according to Saytzeff rule, is major product.

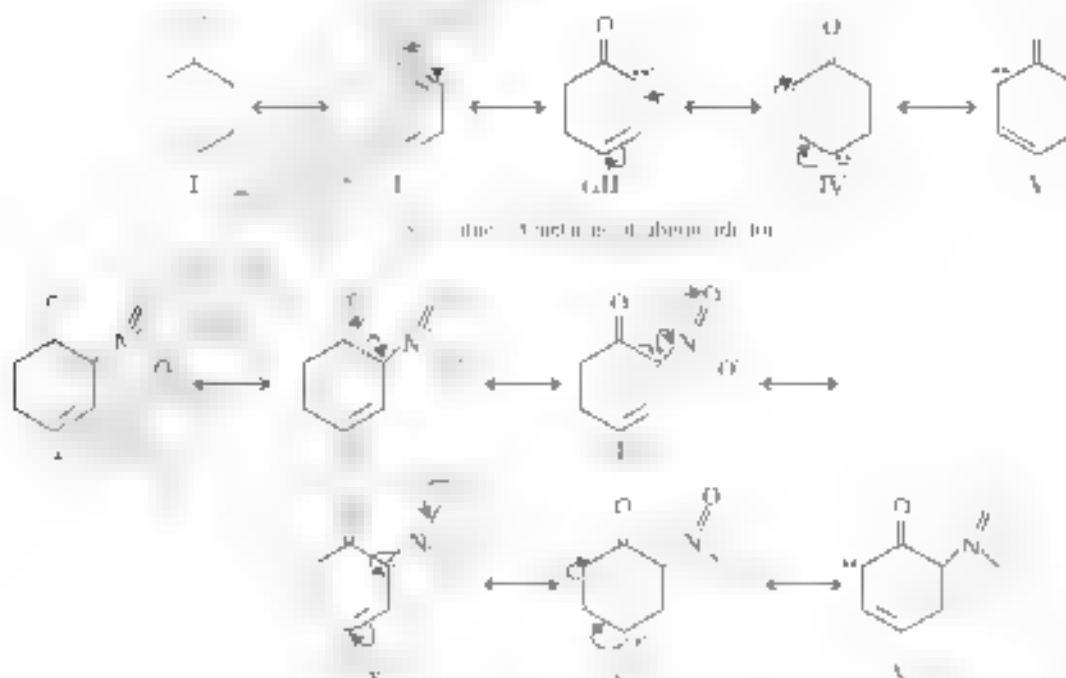


(ii) The acid-catalysed dehydration of butan-1-ol produces but-2-ene as the major product and but-1-ene as the minor product. This is because dehydration of an alcohol occurs through the formation of carbocation intermediates. During the reaction it first forms 1° carbocation I which undergoes 1,2-hydride shift to form 2° carbocation II. This then loses a proton to form more stable but-2-ene instead of but-1-ene. This is because but-2-ene is more stable and according to Saytzeff rule is preferably formed.

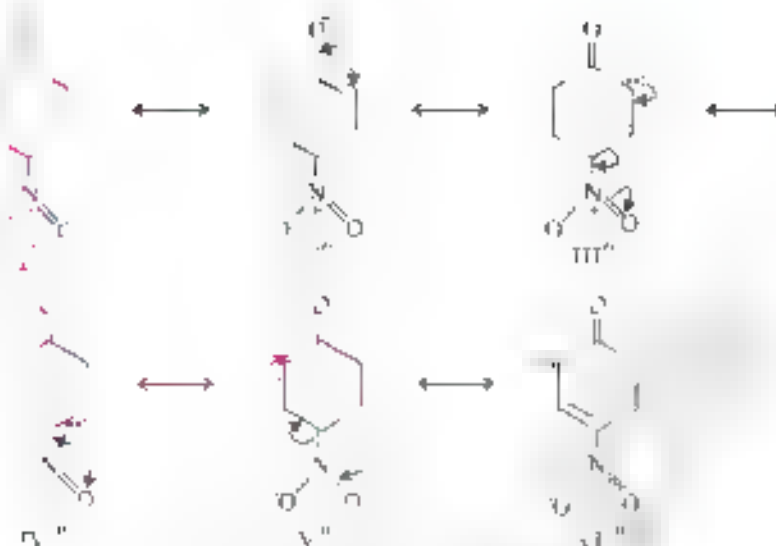


Q.8. *Ortho* and *para* nitrophenols are more acidic than phenol. Draw the resonance structures of the corresponding phenoxide ions.

Ans. The resonating structures of phenoxide ion and *ortho* and *para* nitrophenoxide ions are



Resonance structures of *o*-nitro phenoxide ion

Resonance structures of *p*-nitrophenoxide ion

It is clear from the above structures that due to $-I$ effect of NO_2 group, *o*- and *p*-nitrophenoxide ions are more stable because they have additional resonance structures IV and V, than phenoxide ion. Hence *o*- and *p*-nitrophenols are more acidic than phenol.

Q.9. Write the equations involved in the following reactions.

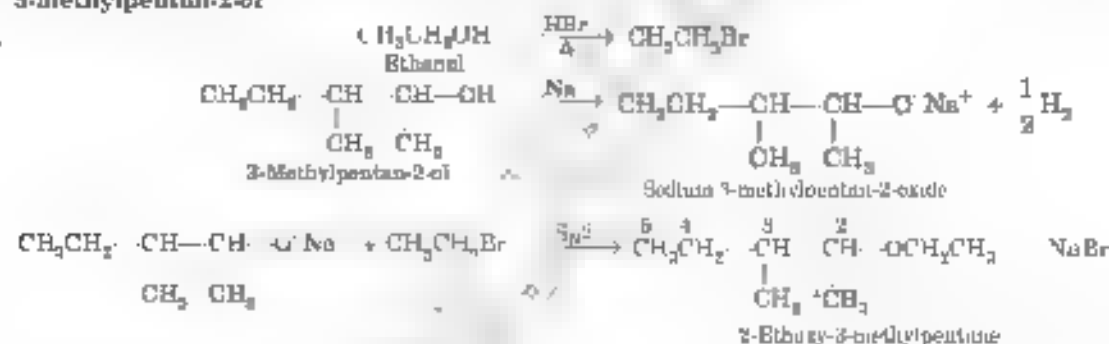
(i) Reimer-Tiemann reaction

(ii) Kulbe's reaction

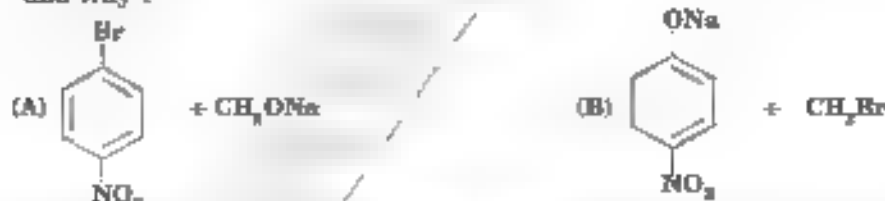
Ans. Refer special reactions of phenols (i, 3 and (ii), 1 (Text Book page 40-41).

Q.10. Write the reactions of Williamson synthesis of 2-ethoxy-3-methylpentane starting from ethanol and 3-methylpentan-2-ol

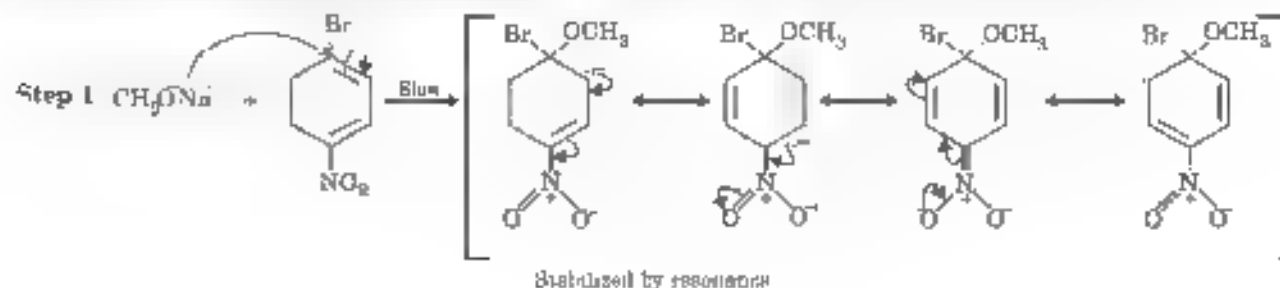
Ans.




Q.11. Which of the following is an appropriate set of reactants for the preparation of 1-methoxy-4-nitrobenzene and why?



Ans. Chemically both sets are equally probable. In set A, the Br group is activated by the electron withdrawing effect of NO_2 group. Therefore, nucleophilic attack of CH_3O^- on Br is followed by elimination of $NaBr$ gives the desired ether.







 $\xrightarrow[\text{DMF}]{\text{NaOMe}}$

 1-Methoxy-4-nitrobenzene



 sodium 4-nitrophenoxide + CH_3Br $\xrightarrow{\text{BHA}}$ 4-methoxy-1-nitrobenzene

(i) $\text{CH}_3-(\text{CH}_2)_4-\text{H}_2\text{O}-\text{CH}_2 + \text{HBr} \rightarrow$ (ii)  + HBr

(iii)  $\xrightarrow[\text{Conc. HNO}_3]{\text{Conc. H}_2\text{SO}_4}$ (iv) $(\text{CH}_3)_3\text{C}-\text{OC}_2\text{H}_5 \quad \text{II}$

Both the alkyl groups attached to O atom are geminal and therefore attack of Br⁻ ion occurs on the smaller methyl

$$U \text{ (benzene ring with } -OC_2H_5) + HEr \rightarrow \text{benzene ring with } -OH + C_2H_5Er$$
$$\text{CH}_3\text{C}(\text{CH}_3)_2\text{OCH}_2\text{CH}_3 + \text{H}^+ \rightarrow \text{CH}_3\text{C}(\text{CH}_3)_2\text{O}^+\text{CH}_2\text{CH}_3 + \text{CH}_3\text{CH}_2\text{OH}$$

tert Butyl cation Ethanol

When one of the groups in an unsymmetrical ether is tertiary then the halide formed is tertiary halide.

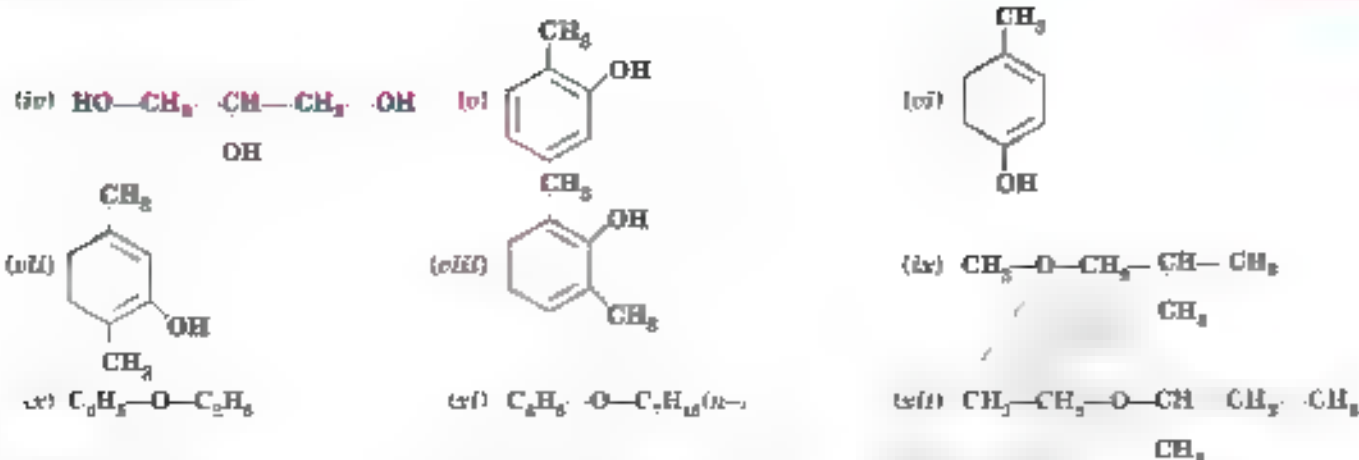


NCERT

Textbook Exercises

Q.1. Write IUPAC names of the following compounds :





Ans. 2,2,4-Trimethylpentan-3-ol

(iv) Propane-1,2,3-triol

(v) 3,5-Dimethylphenol

x Ethoxybenzene

Q.2 Write structures of the compounds whose IUPAC names are as follows

(i) 2-Methylbutan-2-ol

(ii) 2,3-Diethylphenol

(iii) Cyclohexylmethanol

(x) 3-Chloromethylpentan-1-ol

(v) 5-Ethylheptan-2,4-diol

(vi) 2-Methylphenol

(vii) 2,6-Dimethylphenol

(x) 1-Phenoxyheptane

(v) Butane-2,3-diol

(vi) 4-Methylphenol

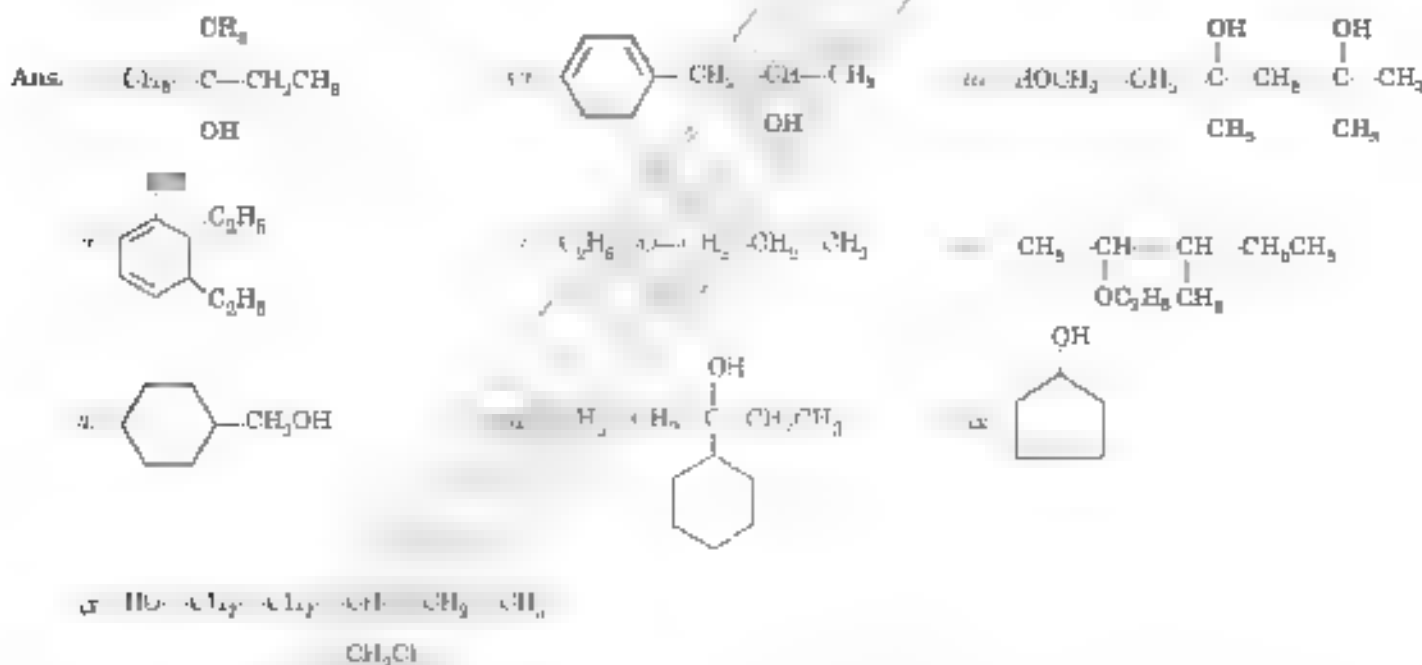
(x) 1-Methoxy-2-methylpropane

(xi) 2-Ethoxybutane

(iii) 3,5-Dimethylhexane-1,3,5-triol

(iv) 2-Ethoxy-3-methylpentane

(ix) Cyclopent-3-en-1-ol



Q.3 (a) Draw the structures of all isomeric alcohols of molecular formula $\text{C}_6\text{H}_{14}\text{O}$ and give their IUPAC names.

(b) Classify the isomers of alcohols in question 3(a) as primary, secondary and tertiary alcohols.

Ans. Refer Solved Example 1 (Page 8).

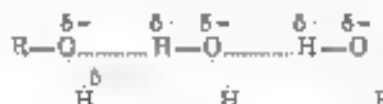
Q.4 Explain why propanol has higher boiling point than that of the hydrocarbon, butane?

Ans. The molecules of propanol are held together by intermolecular hydrogen bonding while butane molecules have only weak van der Waals forces of attraction. Since hydrogen bonds are stronger than van der Waals forces, therefore, propanol has higher boiling point than butane.



Q.5. Alcohols are comparatively more soluble in water than hydrocarbons of comparable molecular masses. Explain this fact.

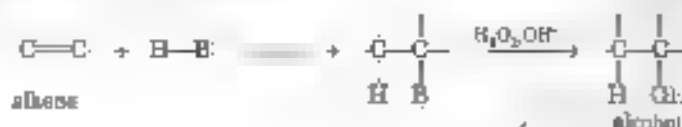
Ans. Alcohols can form hydrogen bonds with water and break the hydrogen bonds existing between water molecules. Hence, they are soluble in water.



On the other hand, hydrocarbons cannot form hydrogen bonds with water molecules and hence are insoluble in water.

Q.6. What is meant by hydroboration-oxidation reaction? Illustrate it with an example.

Ans. The addition of diborane to alkenes to form trialkylboranes followed by their oxidation with alkaline hydrogen peroxide to form alcohols is called hydroboration-oxidation reaction.

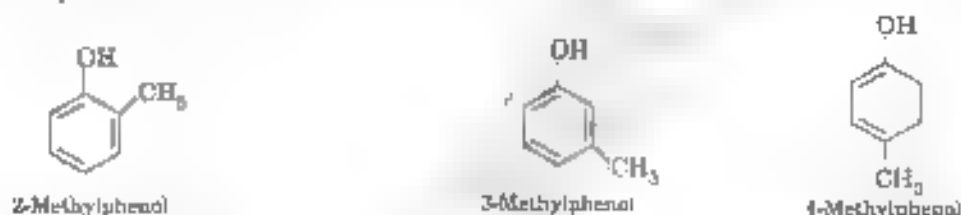


For example,



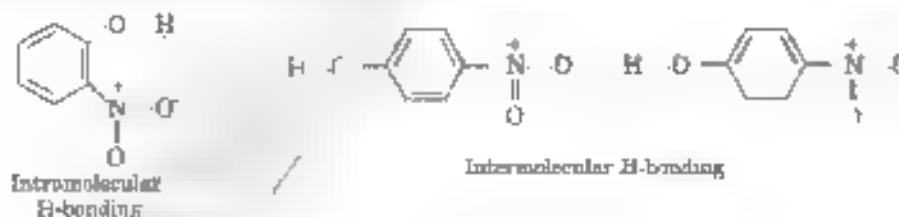
Q.7. Give the structures and IUPAC names of monohydric phenols of molecular formula, $\text{C}_7\text{H}_8\text{O}$.

Ans. Three isomers are possible

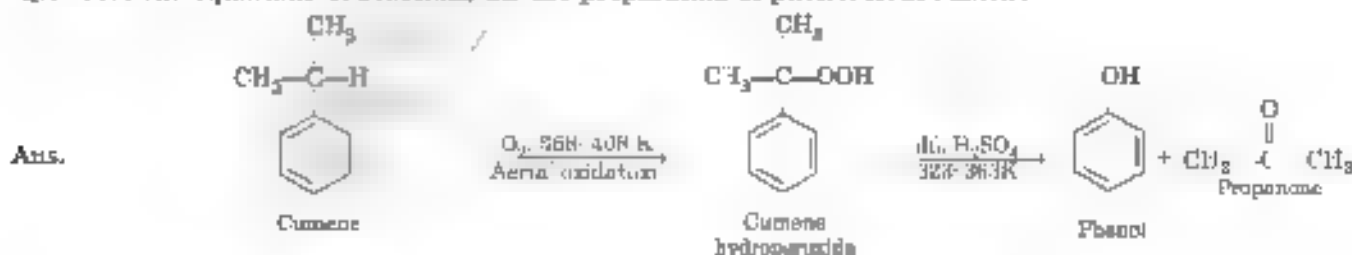


Q.8. While separating a mixture of *ortho* and *para* nitrophenols by steam distillation, name the isomer which will be steam volatile. Give reason.

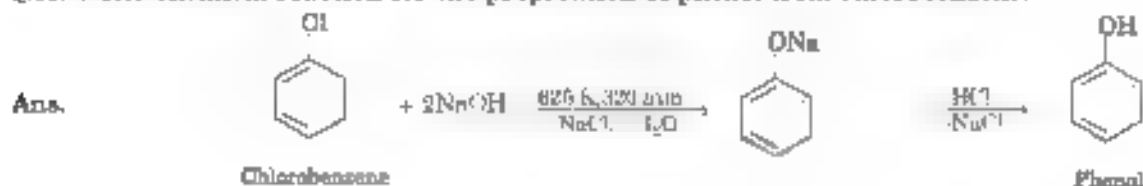
Ans. *o*-Nitrophenol is steam volatile due to chelation because of intramolecular hydrogen bonding. In the other hand, *p*-nitrophenol is not steam volatile because of intermolecular hydrogen bonding. Hence *o*-nitrophenol can be separated from *p*-nitrophenol by steam distillation.



Q.9. Give the equations of reactions for the preparation of phenol from cumene.

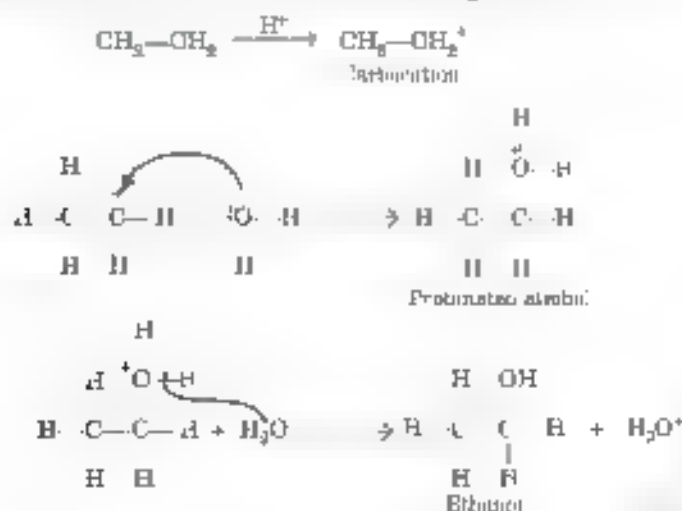


Q.10. Write chemical reaction for the preparation of phenol from chlorobenzene.



Q.1. Write the mechanism of hydration of ethene to yield ethanol.

Ans. It is an example of electrophilic addition. The water molecule with a little polarity is not in a position to give H⁺ for the initial attack. Therefore it is an acid catalysed reaction. The H⁺ of the acid initially attacks the alkene to form carbocation which then takes up an electron pair from H₂O molecule.

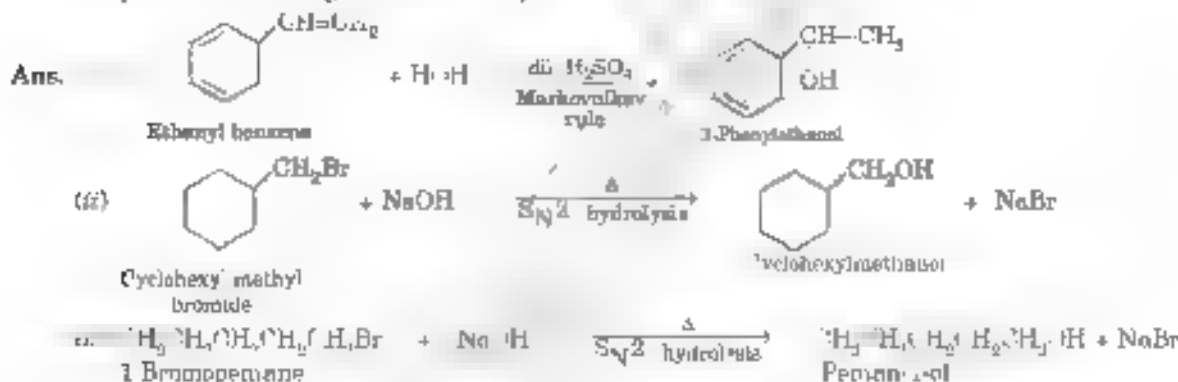


Q.12. You are given benzene, conc. H₂SO₄ and NaOH. Write the equations for the preparation of phenol using these reagents.



Q.13. Show how will you synthesize

- 1-phenylethanol from a suitable alkene,
- cyclohexylmethanol using an alkyl halide by an S_N2 reaction,
- pentan-1-ol using a suitable alkyl halide?



Q.14. Give two reactions that show the acidic nature of phenol. Compare acidity of phenol with that of ethanol.

Ans. The reactions showing acidic character of phenol are

- Reaction with sodium. Phenol reacts with sodium to give H₂ gas



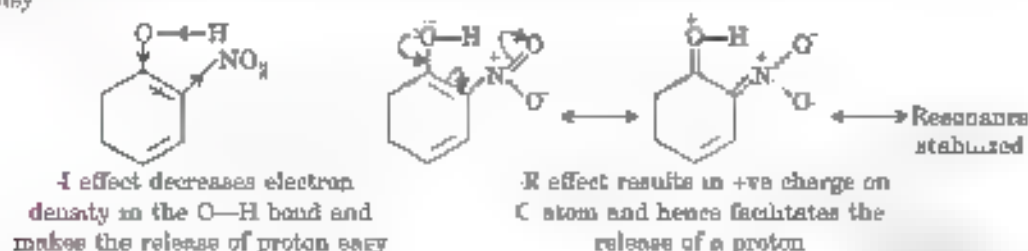
- Reaction with NaOH. Phenol dissolves in NaOH to give sodium phenoxide and water



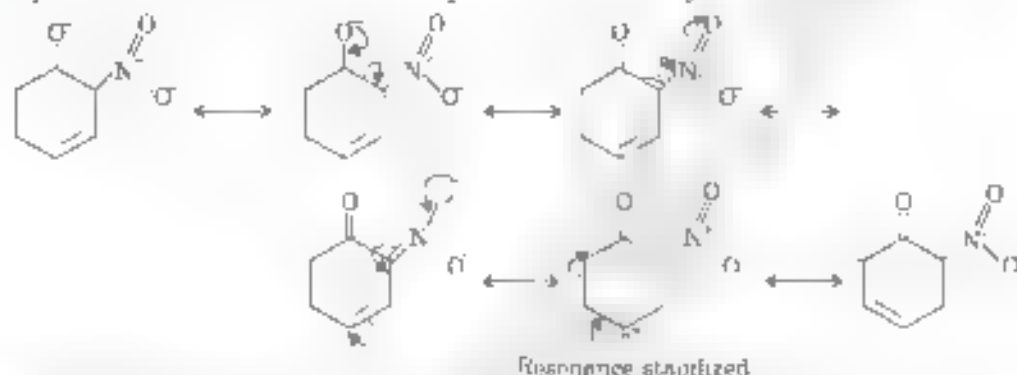
Phenol is more acidic than ethanol because of more resonance stabilized structures of phenoxide. Refer Text Book page 32-34.

Q.15. Explain why is *ortho* nitrophenol more acidic than *ortho* methoxyphenol ?

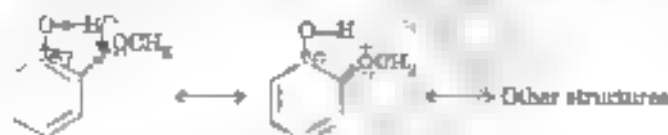
Ans. Due to strong $-R$ and $-I$ effect of NO_2 group electron density in $O-H$ bond decreases and hence the loss of a proton becomes easy



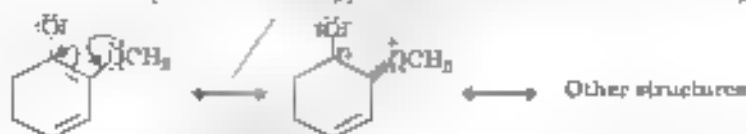
Moreover the *o*-nitrophenoxide formed after the loss of a proton is stabilized by resonance.



o-nitrophenoxide ion is stabilized by resonance and hence *o*-nitrophenol is a stronger acid. On the other hand, due to $+R$ effect of the $+OCH_3$ group the electron density in the $O-H$ bond increases and thus makes the loss of proton difficult.



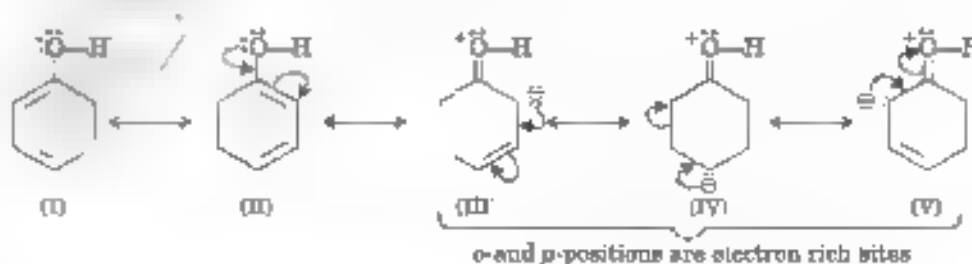
Furthermore, after the loss of proton *o*-methoxyphenoxide ion left is destabilized by resonance.



The two negative charges repel each other and therefore destabilize the *o*-methoxyphenoxide ion. Thus, *o*-nitrophenol is more acidic than *o*-methoxyphenol.

Q.16. Explain how does the $-OH$ group attached to a carbon of benzene ring activate it towards electrophilic substitution ?

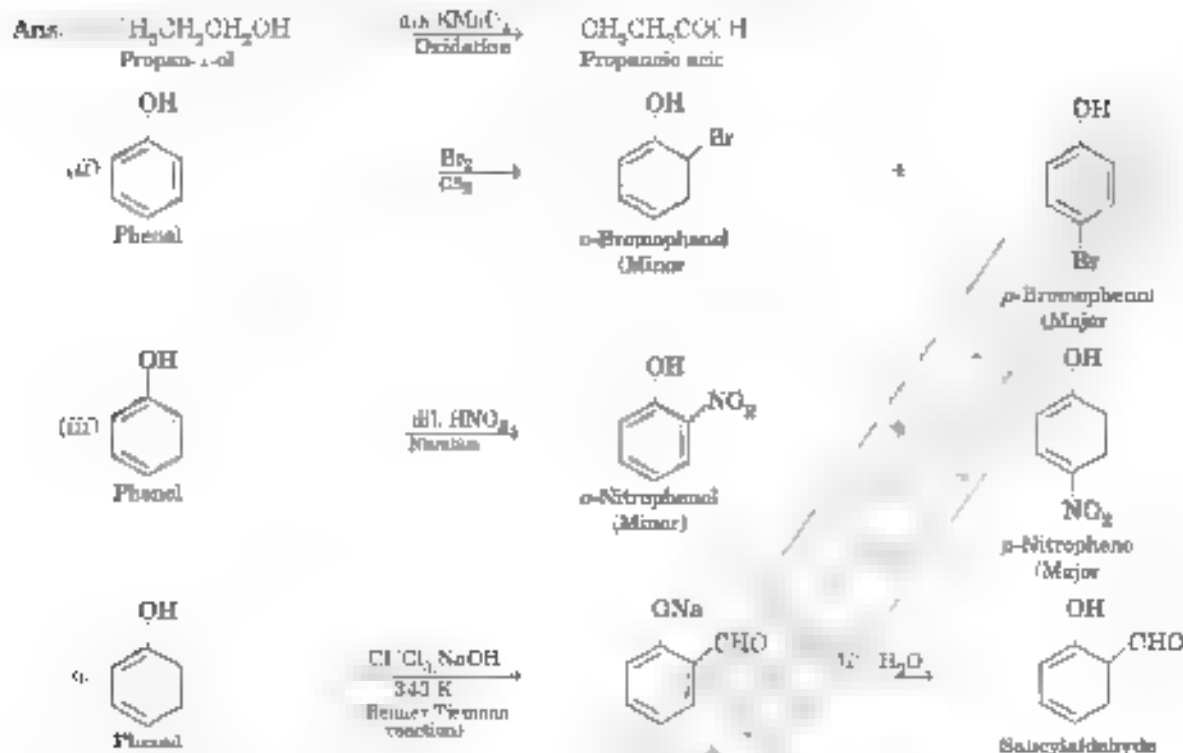
Ans. Phenol is a resonance hybrid of the following structures.



As a result of $+R$ effect of the $-OH$ group, the electron density in the benzene ring increases and thereby facilitating the attack of the electrophile. Hence presence of $-OH$ group activates the benzene ring towards electrophilic substitution reaction. This is because the $-OH$ group is an activating group, these reactions occur at a faster rate than reactions of benzene itself. Further it is clear from the resonating structures the electron density is relatively higher at *o*- and *p*-positions and therefore electrophilic substitution occurs preferentially at *o*- and *p*-positions. Thus the $-OH$ group is *ortho-para* directing and therefore incoming group comes at *ortho* or *para* position.

Q.17. Give equations of the following reactions :

- Oxidation of propan-1-ol with alkaline KMnO_4 solution.
- Bromine in CS_2 with phenol.
- Dilute HNO_3 with phenol.
- Treating phenol with chloroform in presence of aqueous NaOH .



Q.18. Explain the following with an example :

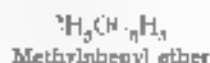
- Kolbe's reaction
- Williamson ether synthesis
- Reimer-Tiemann reaction
- Unsymmetrical ether

Ans. (i) Refer special reactions of phenol, reaction 1 (Text Book Page 40)

(ii) Refer special reactions of phenols, reaction 2 (Text Book Page 41)

(iii) Refer general methods of preparation of ether, reaction 2 (Text Book Page 60)

- If the alkyl or aryl groups attached to the O-atom of the ethers are different, ethers are called unsymmetrical ethers. For example

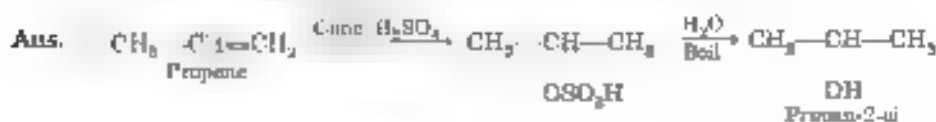


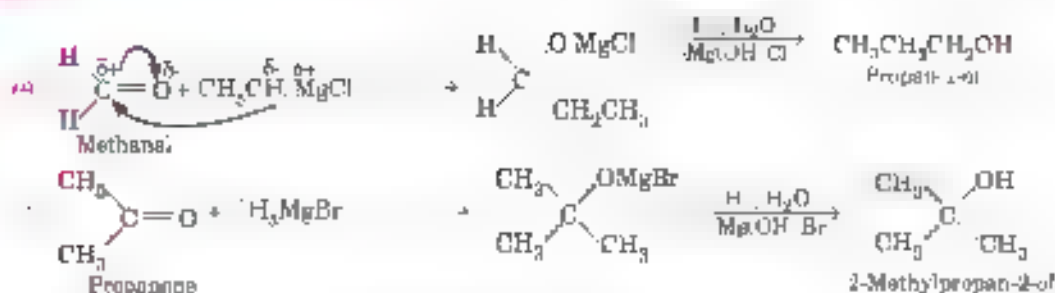
Q.19. Write mechanism of acid dehydration of ethanol to yield ethane.

Ans. Refer Text Book Page 39

Q.20. How are the following conversions carried out ?

- Propene \rightarrow Propan-2-ol
- Benzyl chloride \rightarrow Benzyl alcohol
- Ethyl magnesium chloride \rightarrow Propan-1-ol
- Methyl magnesium bromide \rightarrow 2-Methylpropan-2-ol





Q.21. Name the reagents used in the following reactions :

- Oxidation of a primary alcohol to carboxylic acid
- Oxidation of a primary alcohol to aldehyde
- Bromination of phenol to 2,4,6-tribromophenol
- Benzyl alcohol to benzoic acid
- Dehydration of propan-2-ol to propene
- Butan-2-one to butan-2-ol

Ans. (i) Acidified $\text{K}_2\text{Cr}_2\text{O}_7$ or KMnO_4

(ii) Pyridinium chlorochromate (PCC) in CH_2Cl_2 or Pyridinium dichromate (PDC) in CH_2Cl_2

(iii) Aqueous Br_2 i.e., $\text{Br}_2/\text{H}_2\text{O}$

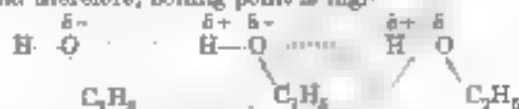
(iv) Acidified or alkaline KMnO_4 followed by hydrolysis with dil. H_2SO_4

(v) Conc. H_2SO_4 at 443 K

(vi) NaBH_4 or Ni/H_2

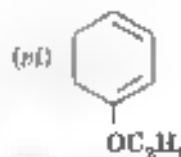
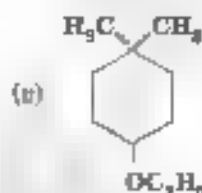
Q.22. Give reason for the higher boiling point of ethanol in comparison to methoxymethane.

Ans. The boiling point of ethanol is higher than methoxy methane because of the presence of strong intermolecular hydrogen bonding between ethanol molecules. Because of hydrogen bonding energy has to be supplied to overcome the forces of attraction between molecules and therefore, boiling point is high.



However, no such hydrogen bonding exists in methoxymethane.

Q.23. Give IUPAC names of the following ethers :



Ans. I-Methoxy-2-methylpropane

(ii) 1-Methoxypropane

(iii) 2-chloro-1-methoxyethane

(iv) Ethoxy-1,1-dimethylcyclohexane

(v) 4-Nitroanisole

(vi) Ethoxybenzene

Q.24. Write the names of reagents and equations for the preparation of the following ethers by Williamson's synthesis:

(i) 1-Propoxypropane

(ii) Ethoxybenzene

(iii) 2-Methoxy-2-methylpropane

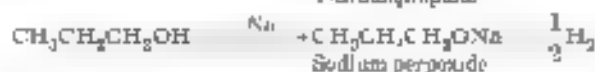
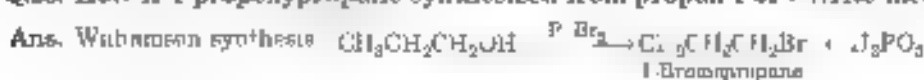
(iv) 1-methoxyethane

Ans. Refer Solved Example 17 (Page 87)

Q.25. Illustrate with examples the limitations of Williamson synthesis for the preparation of certain types of ethers.

Ans. Refer Text Book Page 85

Q.26. How is 1-propoxypropane synthesized from propan-1-ol? Write mechanism of this reaction.

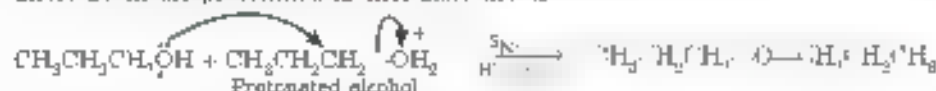


It can also be prepared by dehydration of propan-1-ol with conc. H_2SO_4 at 413 K.

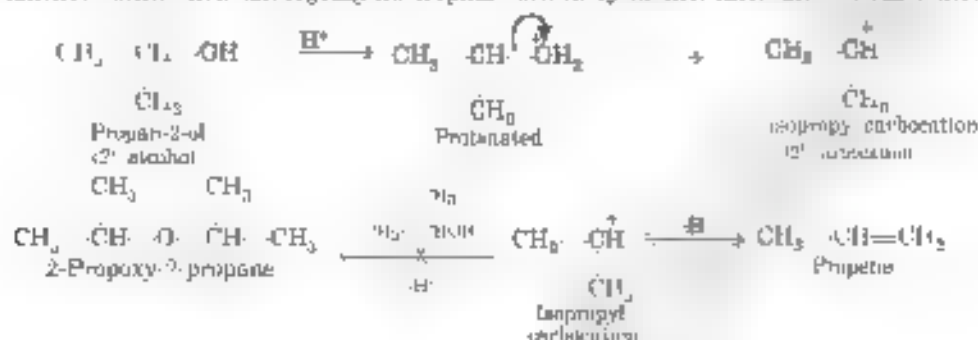


Q.27. Preparation of ethers by acid dehydration of secondary or tertiary alcohols is not a suitable method. Give reason.

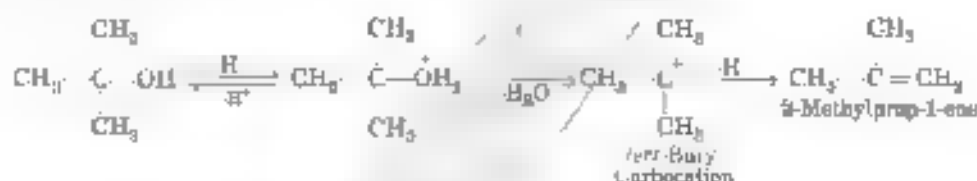
Ans. Acid-catalysed dehydration of 1° alcohols to ethers takes place by S_N2 reaction involving nucleophilic attack by the alcohol molecule on the protonated alcohol molecule as



However, under these conditions, 2° and 3° alcohols give α -kenes rather than ethers. This is because of the steric hindrance, nucleophilic attack by the alcohol on the protonated alcohol molecule does not take place. Instead of this, the protonated 2° and 3° alcohols lose a molecule of water to form stable 2° and 3° carbocations. These carbocations then prefer to lose a proton to form alkenes rather than undergoing nucleophilic attack by alcohol molecule to form ethers.

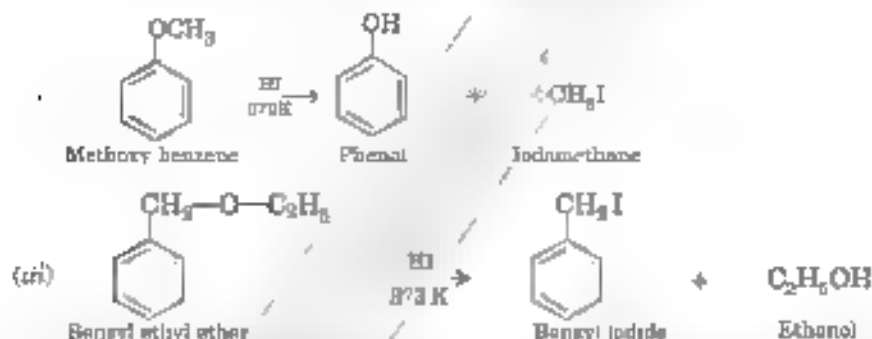


Similarly, 2° alcohols give alkenes



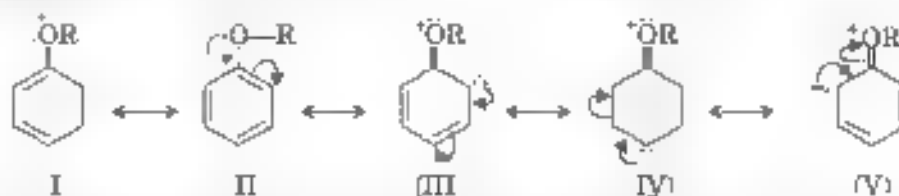
Q.28. Write the equation of the reaction of hydrogen iodide with

(f) 1-propoxypropane, (h) methoxybenzene and (ff) benzyl ethyl ether.



Q.29 Explain the fact that in aryl alkyl ethers (i) the alkoxy group activates the benzene ring towards electrophilic substitution and (ii) it directs the incoming substituents to *ortho* and *para* position in benzene ring.

Ans. The alkoxy group increases the electron density on the benzene ring and therefore activates the aromatic ring towards electrophilic substitution reaction as given below



As is clear structures III, IV and V show high electron density at *ortho* and *para* positions and therefore, direct the incoming substituents to *o*- and *p*-position in the benzene ring.

Q.30. Write mechanism of the reaction of HI with methoxymethane.

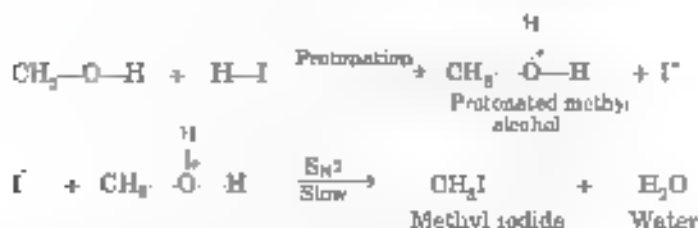
Ans. Step 1. Ether molecule gets protonated



Step 2. The protonated ether undergoes $\text{S}_{\text{N}}2$ attack by I^- ion



If HI is in excess, the methanol formed in step 2 is also converted into methyl iodide as



Q.31. Write equations of the following reactions.

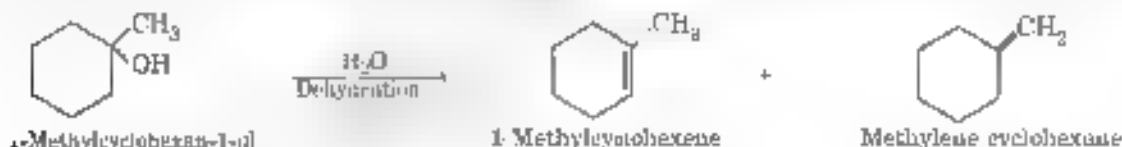
- Friedel Crafts reaction alkylation of anisole
- Nitration of anisole
- Bromination of anisole in ethanoic acid medium
- Friedel Craft's acetylation of anisole

Ans. Refer ring substitution reactions of aromatic ethers Text Book Page 23-24

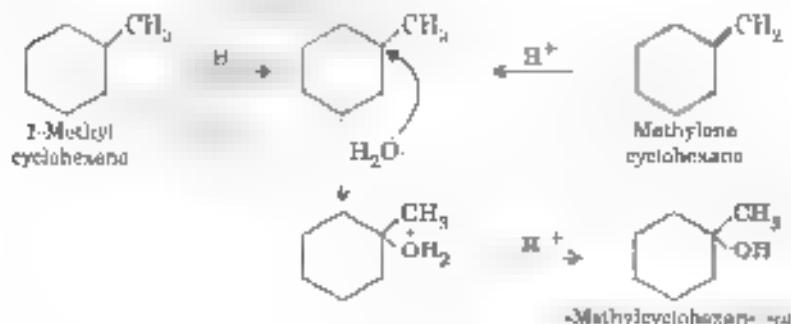
Q.32. Show how would you synthesize the following alcohols from appropriate alkenes?



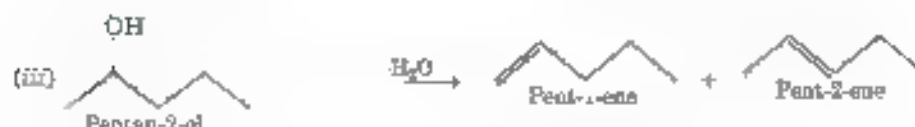
Ans. The alkenes for synthesising the alcohols can be predicted by first dehydrating the alcohol to give single alkene or a mixture of alkenes. If a mixture of alkenes is possible, then find out which alkene gives the desired alcohol. It must be remembered that acid catalysed addition of H_2O to alkenes occurs in accordance with Markovnikov's rule.



The desired alcohol can be obtained by addition of H_2O to either of these.



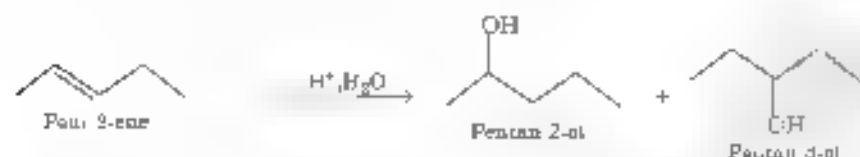
Addition of water in the presence of an acid gives the desired alcohol



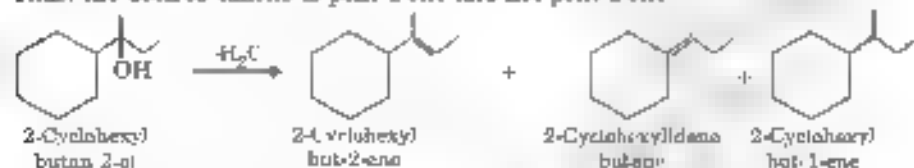
Addition of H_2O to pent-1-ene gives the desired alcohol



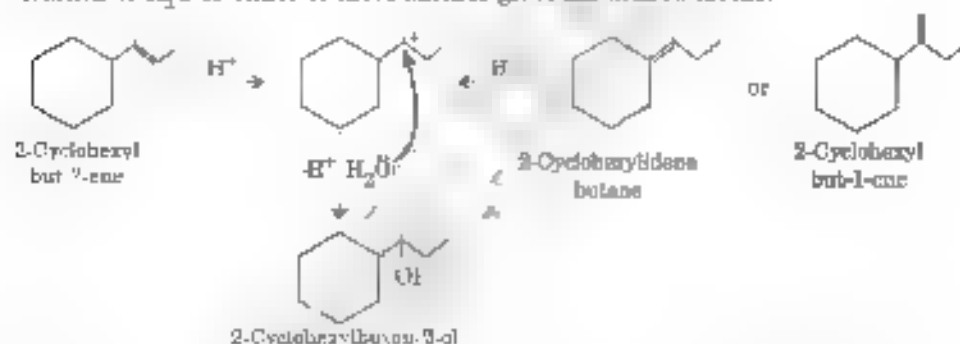
However pent-2-ene will give two products



Thus, the desired alkene is pent-1-ene and not pent-2-ene



Addition of H_2O to either of these alkenes gives the desired alcohol



Q.88. When 2-methylbutan-2-ol is treated with HBr following reaction takes place

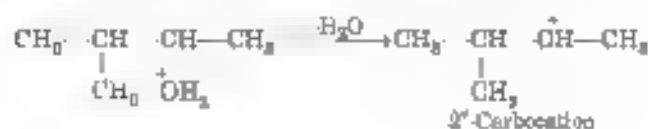


Give a mechanism for this reaction.

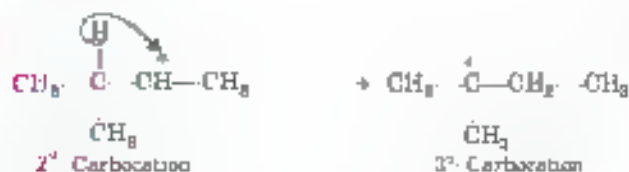
Ans. — Alcohol gets protonated



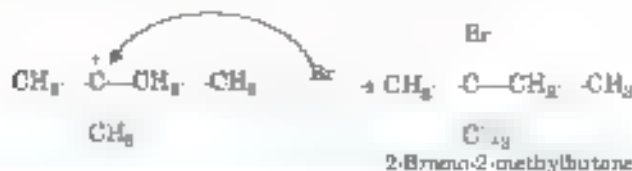
1. Protonated alcohol loses H_2O molecule to form 2° carbocation



(iv) 1, 2-hydride shift of 2-carbocation gives more stable 3° carbocation



(v) Nucleophilic attack by Br⁻ ion gives alkyl halide



NCERT

Exemplar Problems

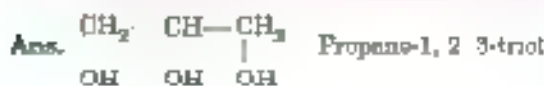
Subjective Questions

Notes:

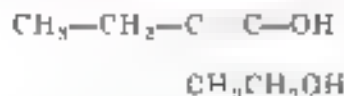
Objective Questions from Exemplar Problems are given in Competition File, page 131

II. Short Answer Type Questions

Q.1. What is the structure and IUPAC name of glycerol?



Q.2. Write the IUPAC name of the compound given below.



Ans. 3-Methylpent-2-ene-1, 3-diol

Q.3. Name the factors responsible for the solubility of alcohols in water.

Ans. The factors responsible for the solubility of alcohols in water are:

- Hydrogen bonding
- a) Size of alkyl or aryl group

Q.4. What is denatured alcohol?

Ans. It is 95% ethyl alcohol. To avoid misuse of alcohol for drinking it is made unfit by mixing some copper sulphate and pyridine in it. This is called denatured alcohol.

Q.5. Suggest a reagent for the following conversion.



Ans. Pyridinium chlorochromate, $\text{CrO}_2 \cdot \text{C}_5\text{H}_5\text{N} \cdot \text{HCl}$

Q.6. Out of 2-chloroethanol and ethanol which is more acidic and why?

Ans. 2-Chloroethanol is more acidic because of -I effect of chlorine atom.

Q.7. Suggest a reagent for conversion of ethanol to ethanal.

Ans. Pyridinium chlorochromate, $\text{CrO}_2 \cdot \text{C}_5\text{H}_5\text{N} \cdot \text{HCl}$

Q.8. Suggest a reagent for conversion of ethanol to ethanoic acid.

Ans. Any oxidising agent e.g. acidified KMnO_4 , acidified $\text{K}_2\text{Cr}_2\text{O}_7$

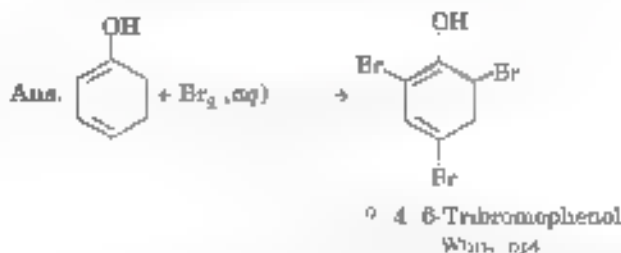
Q.9. Out of o-nitrophenol and p-nitrophenol, which is more volatile? Explain.

Ans. Ortho-nitrophenol is more volatile because there is intramolecular hydrogen bonding in o-nitrophenol. p-Nitrophenol has intermolecular hydrogen bonding.

Q.10. Out of o-nitrophenol and o-cresol, which is more acidic?

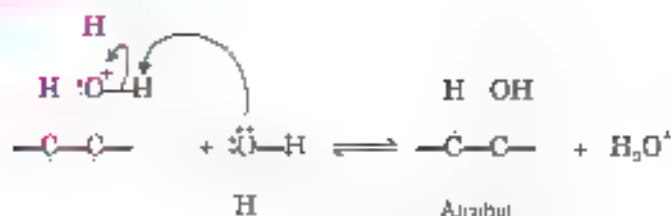
Ans. o-Nitrophenol because nitro group is electron withdrawing group and it increases acidic strength.

Q.11. When phenol is treated with bromine water, white precipitate is obtained. Give the structure and the name of the compound formed.



Q.12. Arrange the following compounds in increasing order of acidity and give a suitable explanation. Phenol, o-nitrophenol, o-cresol.

Ans. Increasing order of acidity
o-Cresol < Phenol < o-Nitrophenol



Q.22. Explain why is $\text{O}=\text{C}=\text{O}$ non-polar while $\text{R}-\text{O}-\text{R}$ is polar.

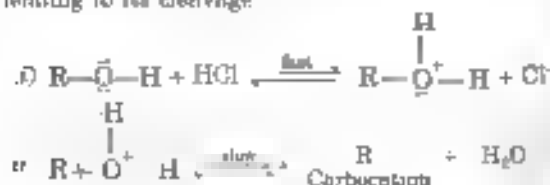
Ans. $\text{O}=\text{C}=\text{O}$ molecule is linear so that the polarities of two $\text{C}=\text{O}$ bonds get cancelled and the molecule is linear.

Ethers have structures similar to water and have angular or bent structure. Therefore, the polarity of two $\text{R}-\text{O}$ groups does not get cancelled and these have net dipole moment. Thus, $\text{R}-\text{O}-\text{R}$ is polar.



Q.23. Why is the reactivity of all the three classes of alcohols with conc. HCl and ZnCl_2 (Lucas reagent) different?

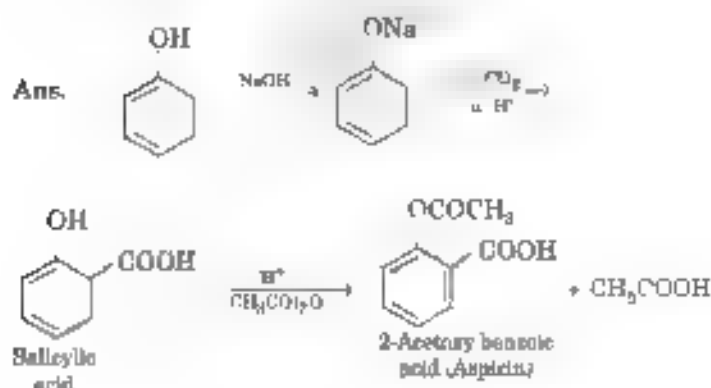
Ans. The alcohols combine with HCl to form protonated alcohol. The positive charge on oxygen weakens the $\text{C}-\text{O}$ bond leading to its cleavage.



The rate determining step in the above mechanism is (ii), which is a slow step reaction. The stability of carbocation will determine the reactivity of the reaction. Since the order of stability of carbocation is

$\text{pri} < \text{sec} < \text{tert}$. Hence the order of formation of alkyl halide in the above reaction is $\text{pri} < \text{sec} < \text{tert}$.

Q.24. Write steps to carry out the conversion of phenol to aspirin.



Q.25. Nitration is an example of aromatic electrophilic substitution and its rate depends upon the group already present in the benzene ring. Out of benzene and phenol, which one is more easily nitrated and why?

Ans. Phenol is more easily nitrated than benzene. The presence of $-\text{OH}$ group in phenol increases the electron density at ortho and para positions in benzene ring by +R effect. Since nitration is an electrophilic substitution reaction, it will be more reactive at position where the electron density is more.

Q.26. In Kolbe's reaction, instead of phenol, phenoxide ion is treated with carbon dioxide. Why?

Ans. Phenoxide ion is more reactive than phenol towards electrophilic aromatic substitution. There it undergoes electrophilic substitution with carbon dioxide which is a weak electrophile.

Q.27. Dipole moment of phenol is smaller than that of methanol. Why?

Ans. In phenol, $\text{C}-\text{O}$ bond is less polar due to electron-withdrawing effect of benzene ring. In methanol, $\text{C}-\text{O}$ bond is more polar due to electron-releasing effect of $-\text{CH}_3$ group. Therefore, phenol is less polar than methanol.

Q.28. Ethers can be prepared by Williamson synthesis in which an alkyl halide is reacted with sodium alkoxide. Di-*tert*-butyl ether can't be prepared by this method. Explain.

Ans. In *tert*-butyl halides, elimination is favoured over substitution, and therefore, alkene is the only reaction product and ether is not formed.

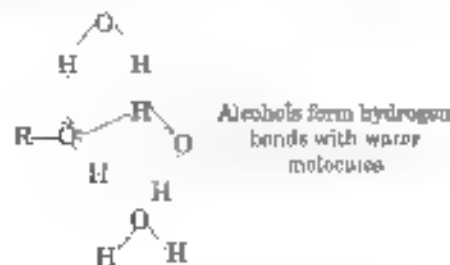
Q.29. Why is the $\text{C}-\text{O}-\text{H}$ bond angle in alcohols slightly less than the tetrahedral angle whereas the $\text{C}-\text{O}-\text{C}$ bond angle in ether is slightly greater?

Ans. The $\text{C}-\text{O}-\text{H}$ bond angle in alcohols is slightly less than the tetrahedral angle (109.5°) because of larger repulsions between the lone pairs of electrons. For example in methanol, $\text{C}-\text{O}-\text{H}$ bond angle is 108.9° .

In ethers, the $\text{C}-\text{O}-\text{C}$ bond angle is slightly greater than tetrahedral angle. For example in dimethyl ether, $\text{C}-\text{O}-\text{C}$ bond angle is 111.7° . The larger bond angle in ethers may be because of greater repulsions between bulkier alkyl groups as compared to one H in alcohols.

Q.30. Explain why low molecular mass alcohols are soluble in water.

Ans. The lower members of alcohols are highly soluble in water but the solubility decreases with increase in molecular weight. The solubility of lower alcohols in water is due to the formation of hydrogen bonds between alcohols and water molecules.



However, as the size of alcohol molecule increases, the alkyl group becomes larger and prevents the formation of hydrogen bonds with water molecules and hence the solubility goes on decreasing with increase in length of carbon chain or molecular mass of alcohol.

Q.81 Explain why *p*-nitrophenol is more acidic than phenol.

Ans. The electron withdrawing group NO_2 withdraws electrons and disperses the negative charge. Therefore, NO_2 group stabilizes the phenoxide ion. Hence *p*-nitrophenol is more acidic than phenol.

Q.82 Explain why alcohols and ethers of comparable molecular mass have different boiling points?

Ans. Ethers have low polarity and as a result do not show any association by intermolecular hydrogen bonding. Therefore, ethers have low boiling points and lower than that of isomeric alcohols and almost same as those of alkanes of comparable molecular masses.

$\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_3$	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$
Diethyl ether	<i>n</i> -Butyl alcohol	<i>n</i> -Pentane
307 K	390 K	309 K

The large difference in boiling points of alcohols and ethers is due to the presence of hydrogen bonding in alcohols.

Q.83 The carbon-oxygen bond in phenol is slightly stronger than that in methanol. Why?

Ans. C—O bond in phenol is stronger than that in methanol due to the fact that

(i) In phenol, conjugation of lone pair of electrons on oxygen with aromatic ring results in partial double bond character in carbon-oxygen bond.

(ii) In phenol, oxygen is bonded to a sp^2 hybridised carbon atom while in methanol, it is bonded to a sp^3 hybridised carbon atom. The bond formed between oxygen and sp^2 hybridised carbon is more stable than that formed between oxygen and sp^3 hybridised carbon.

Q.84 Arrange water, ethanol and phenol in increasing order of acidity and give reason for your answer.

Ans. Increasing order of acidity is: ethanol < water < phenol. The phenoxide ion obtained after the removal of a proton is stabilised by resonance whereas the ethoxide ion obtained after the removal of a proton is destabilised by +I effect of C_2H_5 group. Therefore phenol is stronger acid than ethanol.



On the other hand ethanol is weaker acid than water because electron releasing C_2H_5 group in ethanol increases the electron density on oxygen and hence the polarity of O—H bond in ethanol decreases. This results in the decreasing acidic strength. Hence acidic strength increases in the order given above.



QUICK

MEMORY TEST



A. Say True or False

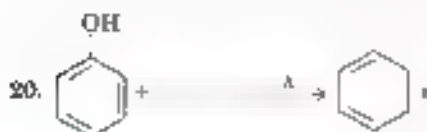
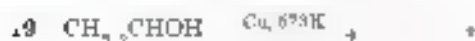
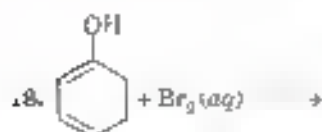
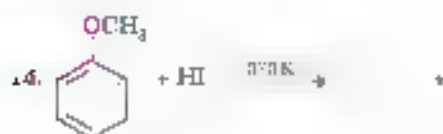
- Ethers are more polar than isomeric alcohols.
- The boiling points of ethers are lower than those of isomeric alcohols.
- Bond angle in diethyl ether is more than in water.
- Sodium ethoxide can be prepared by the reaction of ethanol with aqueous sodium hydroxide.
- tert*-butyl alcohol is more soluble in water than *n*-butyl alcohol.
- m*-methoxyphenol is a weaker acid than phenol.
- 2, 4-dinitrophenol is less acidic than phenol.
- Reactivity of ethanol is less with sodium than that of *iso*-propyl alcohol.
- Alcohols are stronger acids than water.
- Primary alcohols undergo dehydration more easily than secondary and tertiary alcohols.
- Phenols turn blue litmus red.
- Primary alcohols on dehydrogenation give aldehydes.
- Phenetole reacts with HI at 373 K to give ethanol and iodobenzene.
- Acetone reacts with methyl magnesium bromide followed by hydrolysis to give secondary alcohols.
- Reactivity of halogen acids towards ethers follows the sequence



B. Complete the missing links

- Dehydration of ethyl alcohol with conc. H_2SO_4 at 413 K gives
- Lower alcohols are highly soluble in water due to
- 100% pure ethanol is called
- Tertiary alcohol when passed over heated copper at 573 K gives
- Amongst the three isomers of nitrophenol the one that is least soluble in water is
- In the formation of salicylic acid by Reimer-Tiemann reaction, phenol is heated with Ca(OH)_2 in the presence of NaOH
- An enzyme which can convert glucose into ethanol is
- Reaction of phenol with NaOH in the presence of aqueous NaOH is called Schotten-Baumann reaction
- Ortho* and *para* nitrophenols can be separated by distillation
- Phenol forms coloured complexes with neutral
- Absolute alcohol can be prepared from rectified spirit by distillation.
- The lowest molecular mass alcohol which is optically active is

13. The main product obtained when sodium phenoxide is treated with CO_2 at 400 K under 4-7 atm. pressure is



C. Choose the correct alternative

1. *o*-Nitrophenol has lower/higher pK_a value than *m*-nitrophenol
2. $\text{C}_6\text{H}_5\text{OH}$ is weaker/stronger acid than $\text{C}_6\text{H}_{11}\text{OH}$
3. Water is weaker/stronger acid than ethanol
4. Ketones are reduced to 1°/2° alcohols
5. Phenol has smaller/larger dipole moment than methanol
6. Benzene-1, 2, 3-triol is called hydroquinone/pyrogallol
7. Oxirane reacts with Grignard reagent to form primary/secondary alcohol
8. Cumene on serial oxidation and on subsequent hydrolysis gives phenol/phenol
9. Butan-2-ol has higher/lower boiling point than butan-1-ol
10. Ethanol on treatment with conc. H_2SO_4 at 440 K gives ethene/ethanethione
11. Picric acid is obtained by heating phenol in the presence of conc. H_2SO_4 with conc. HNO_3 /conc. HNO_3
12. Treatment of sodium phenoxide with CO_2 at 400 K under a pressure of 4-7 atm followed by acidification gives salicylic acid/anthrylnaldehyde

Answers

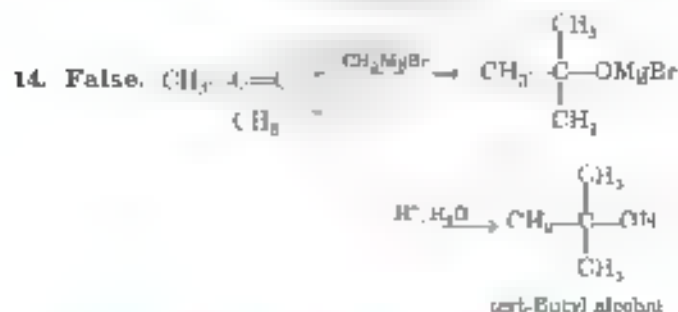
Quick

MEMORY TEST



A. Say True or False

1. False
2. True
3. True
4. False. Ethanol is weaker acid than water and therefore it does not react with aqueous NaOH to form sodium ethoxide
5. True. Solubility increases with branching.
6. False. Due to -I effect of methoxy group at *m*-position, *m*-methoxy phenol is a stronger acid than phenol.
7. False
8. False
9. False
10. False
11. True
12. True
13. False. It gives phenol and ethyl iodide

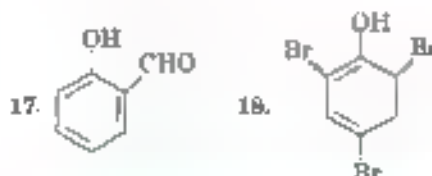


15. True

B. Complete the missing link

1. diethyl ether 2. hydrogen bonding

3. absolute alcohol 4. alkenes 5. *o*-nitrophenol
6. CCl_4 7. zymase 8. benzoyl chloride
9. steam 10. ferric chloride 11. azeotropic



C. Choose the correct alternative

1. lower
2. stronger
3. stronger
4. 2°
5. smaller
6. hydroxy quinol
7. primary
8. phenol
9. lower
10. ethene
11. conc. HNO_3
12. salicylic acid

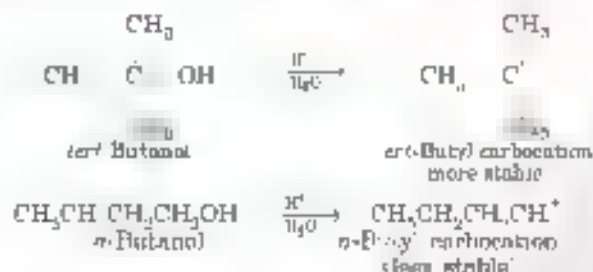
HOTS

Higher Order Thinking Skills & Advanced Level

QUESTIONS WITH ANSWERS

1. Acid-catalysed dehydration of *tert*-butanol is faster than that of *n*-butanol. Explain.

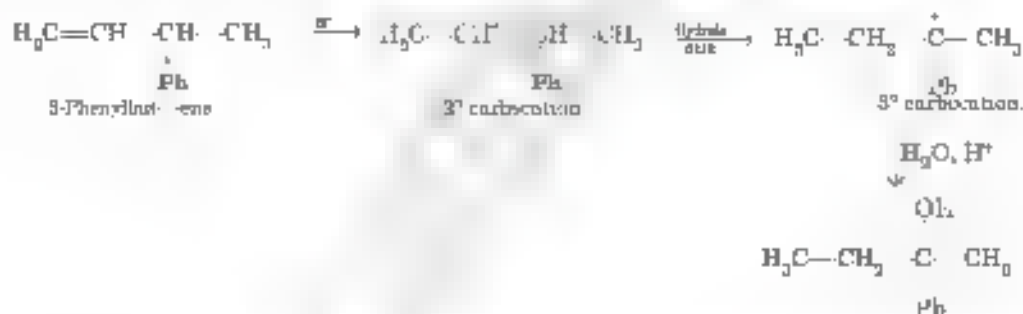
Ans. Acid-catalysed dehydration of alcohols occurs through the formation of carbocation intermediate as



Since *t*-butyl carbocation (3°) is more stable than *n*-butyl carbocation (1°), therefore, acid-catalysed dehydration of *t*-butanol takes place faster than that of *n*-butanol.

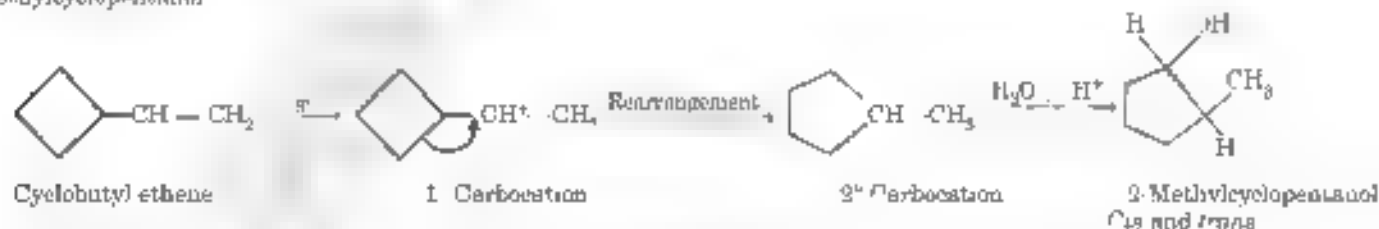
2. Hydration of 3-phenyl-1-butene with dil. H_2SO_4 is not a satisfactory method for preparing 3-phenyl-2-butanol because 2-phenyl-2-butanol is obtained instead. Explain.

Ans. Hydration form 2° carbocation which undergoes a hydride shift to stable benzylic carbocation.

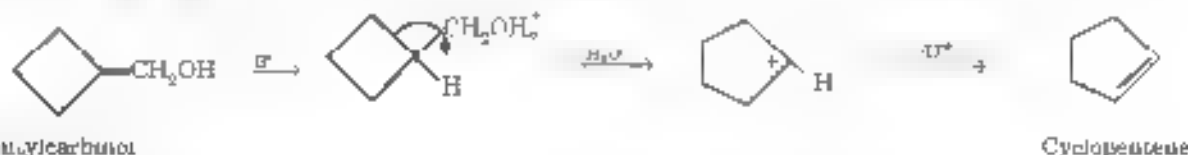


3. Give the product and show the steps in (i) the hydration of cyclobutylethene in dil. H_2SO_4 , (ii) dehydration of cyclobutylcarbinol.

Ans. (i) In this reaction, the addition of H^+ (aq.°) gives a 2° carbocation, which rearranges by ring expansion. Finally it gives 2-methylcyclopentanol.



∴ This reaction results in the expansion of four membered to a five membered ring.



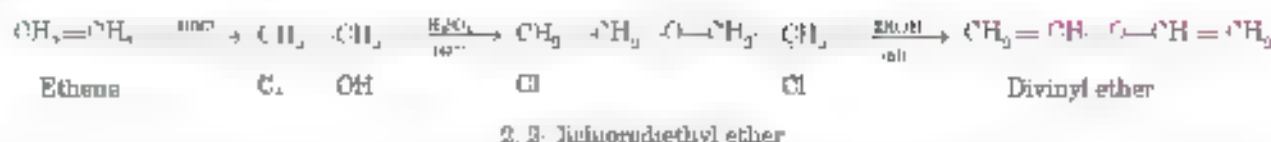
4. Arrange the following alcohols in the increasing order of reactivity with HBr :



Ans. $p\text{-NO}_2\text{C}_6\text{H}_4\text{CH}_2\text{OH} < p\text{-Cl-C}_6\text{H}_4\text{CH}_2\text{OH} < \text{C}_6\text{H}_5\text{CH}_2\text{OH} < \text{C}_6\text{H}_5\text{CHOH} < \text{C}_6\text{H}_5\text{COH}$

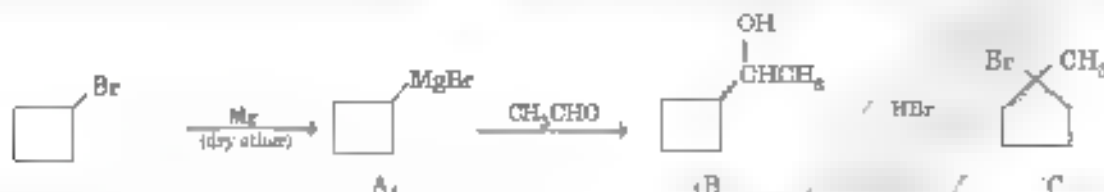
5. Show steps for the conversion of ethene to divinyl ether.

Ans.



6. Cyclobutyl bromide on treatment with magnesium in dry ether forms an organometallic A. The organo-metallic reacts with ethanal to give an alcohol B after mild acidification. Prolonged treatment of alcohol B with an equivalent amount of HBr gives 1-bromo-1-methyl cyclopentane (C). With the structures of A, B and explain how C is obtained from B.

Ans.

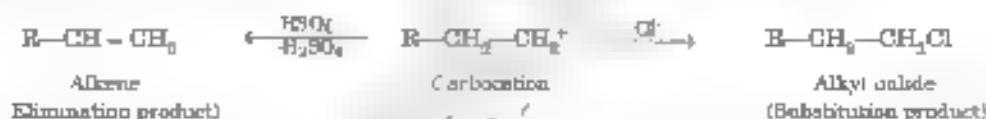


Conversion of B to C occurs as



7 Explain why dehydration of alcohols to form alkenes is always carried out with conc. H_2SO_4 and not with conc. HCl or HNO_3 ?

Ans. Dehydration of alcohols to alkenes occurs through the formation of carbocation intermediate. If HCl is used then chloride Cl^- ion being a good nucleophile will result into substitution reaction forming alkyl chloride.



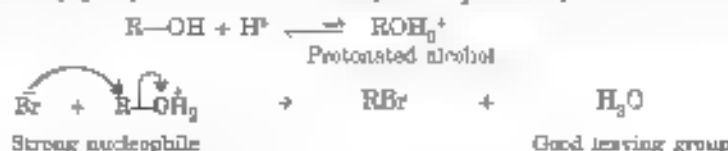
However if H_2SO_4 is used, then the bisulphate HSO_4^- ion being very weak nucleophile cannot result into substitution reaction. Rather the carbocation loses a proton to form elimination product alkene. On the other hand, conc. HNO_3 also cannot be used because it is a strong oxidising agent and will preferentially result into the oxidation of alcohols to aldehydes, ketones or carboxylic acids. Thus the dehydration of alcohols to form alkenes is always carried out with such strong acids H_2SO_4 , H_3PO_4 etc. which have non-nucleophilic anions.

8. Alcohols donot react with NaBr but when H_2SO_4 is added they form alkyl bromides. Explain.

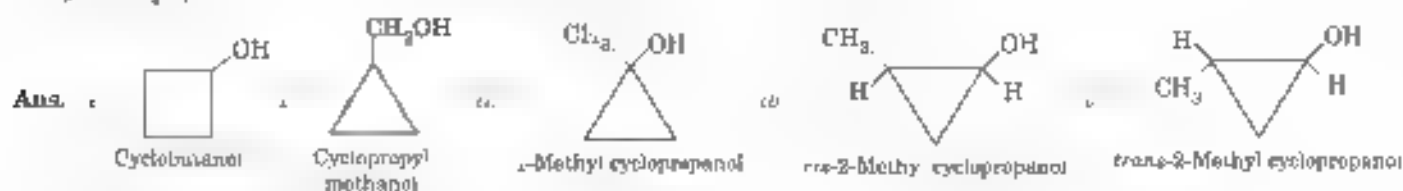


Although Br^- is a strong nucleophile yet OH^- being a strong base is a very poor leaving group. Therefore Br^- cannot displace OH^- from ROH to form RBr . Hence, alcohols donot react with NaBr .

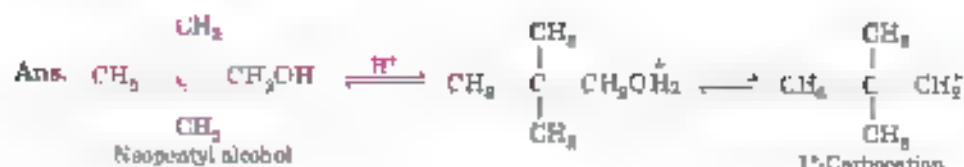
However when H_2SO_4 is added, protonation of alcohols takes place and $-\text{OH}$ group gets converted to $-\text{OH}_2^+$. Since water is a weak base, therefore, $-\text{OH}_2^+$ is a good leaving group. Hence Br^- can displace H_2O from protonated alcohol to form RBr .



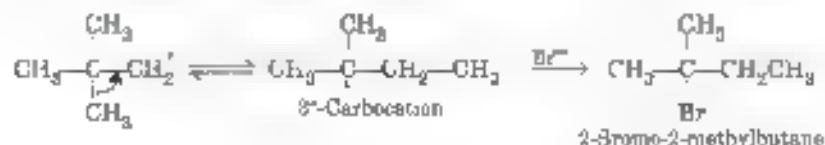
9. Cyclo $\text{C}_4\text{H}_7\text{OH}$ has five isomers. Write their structure and names.



10. Neopentyl alcohol reacts with concentrated HBr to give 2-bromo-2-methylbutane. Write the mechanism for the formation of this product.



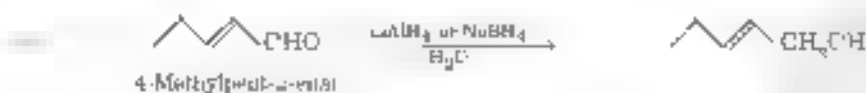
A methyl shift changes 1° carbocation to a stable 3° carbocation



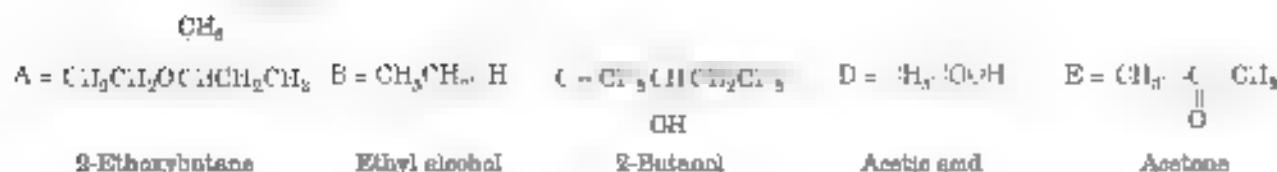
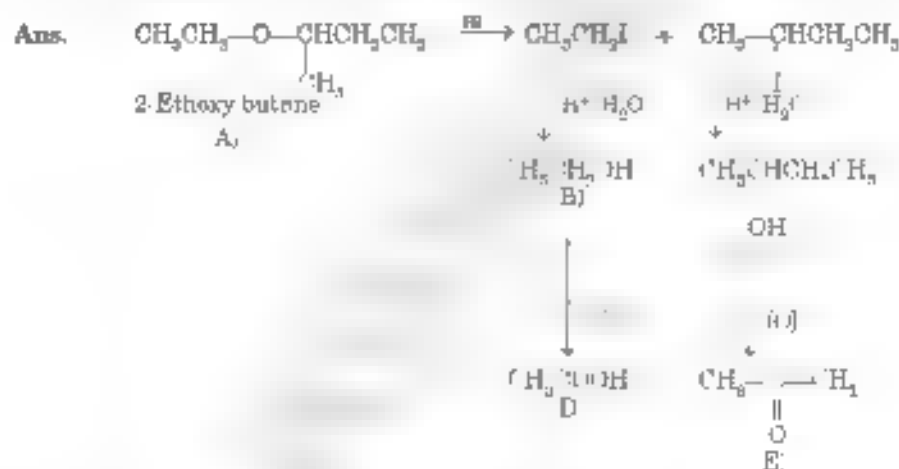
1. Write three carbonyl compounds which may be used to prepare



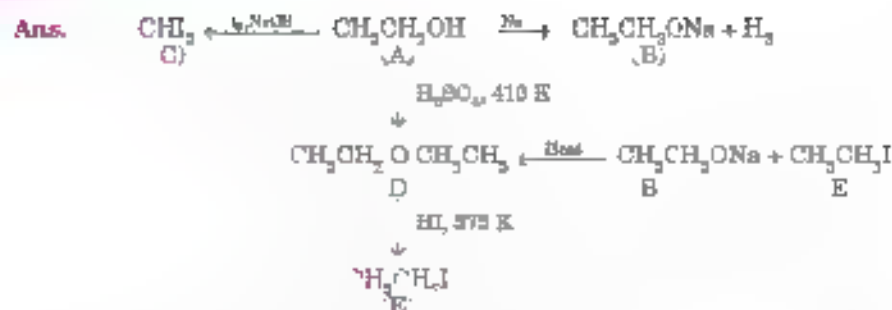
Ans. It can be prepared from an aldehyde, carboxylic acid and ester by reduction with LiAlH_4 , H_2O



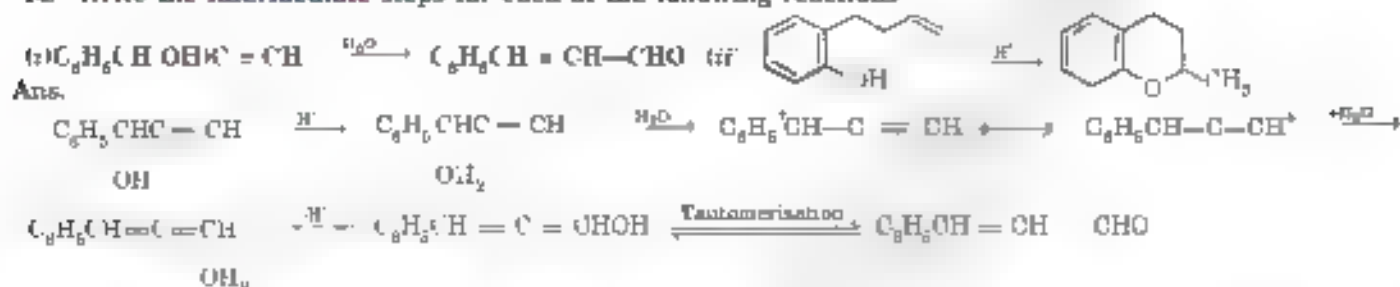
2. An ether A ($\text{C}_6\text{H}_{14}\text{O}$) when heated with excess of hot conc. HI produced two alkyl halides which on hydrolysis form compounds (B) and (C). Oxidation of (B) gave an acid (D) whereas oxidation of (C) gave a ketone (E). Deduce the structural formulae of A, (B), (C), (D) and (E).



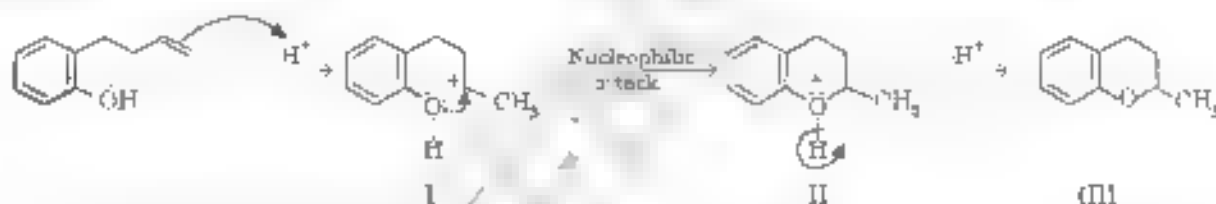
3. An organic compound A ($\text{C}_5\text{H}_{10}\text{O}$) reacts with sodium to form a compound B with the evolution of H_2 and gives a yellow compound C when treated with iodine and NaOH . When heated with conc. H_2SO_4 at 413 K, it gives a compound D ($\text{C}_4\text{H}_8\text{O}$) which on treatment with conc. HI at 373 K gives E. D is also obtained when B is heated with E. Identify A, B, C, D and E and write equations for the reactions involved.



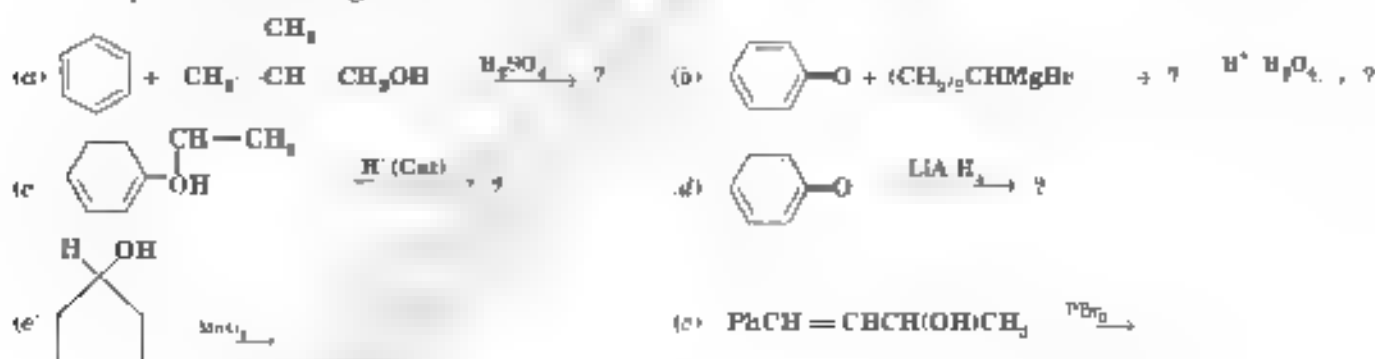
14. Write the intermediate steps for each of the following reactions



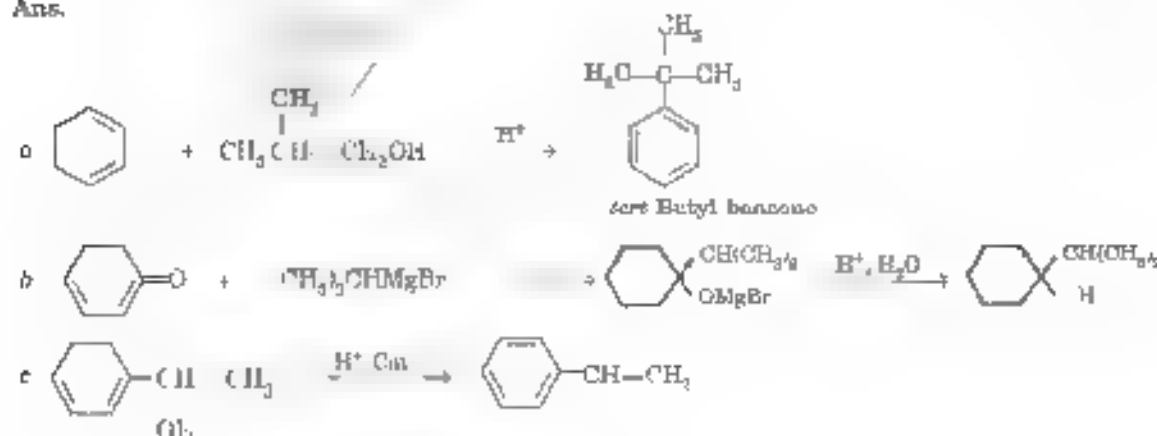
• The addition of H^+ on the double bond takes place in accordance with Markovnikov's rule to form more stable carbocation I. Nucleophilic attack by OH group on I gives the expected product (II) which readily loses a proton to form the final product (III).

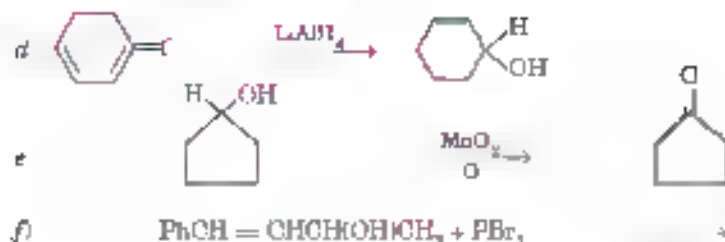


15. Complete the following reactions



Ans.





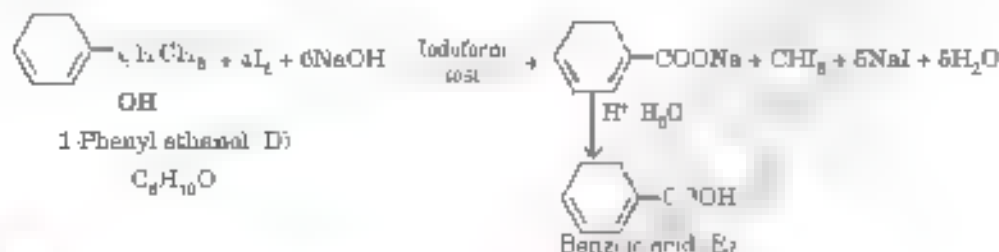
10. A compound $\text{D} (\text{C}_8\text{H}_{10}\text{O})$ upon treatment with alkaline solution of iodine gives a yellow precipitate. The filtrate on acidification gives a white solid $\text{E} (\text{H}_2\text{O}_2)$. Write the structures of D and E and explain the formation of E.

Ans. Since compound $[\text{C}_8\text{H}_{10}\text{O}]$ upon treatment with alkaline solution of I_2 gives yellow ppt. therefore D may be either



The molecular formula of D suggests it to be 1-phenyl ethanol $\text{C}_6\text{H}_5\text{CH(OH)CH}_3$

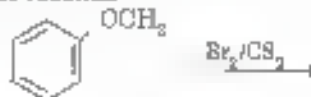
The reaction may be explained as



Revision Exercises

Very Short Answer Questions (carrying 1 mark)

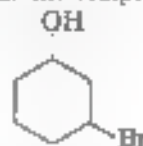
- What is the major product formed when 2-butanol is treated with conc. H_2SO_4 at 443 K?
- What is the order of reactivity of 1°, 2° and 3° alcohols with sodium metal?
- Name the main product obtained when vapour of tert-butyl alcohol are passed over heated copper at 573 K.
- Phenol is heated with CHCl_3 and NaOH at 350 K. What is the product formed? Give the name of the reaction.
- What happens when phenol is warmed with CO_2 in the presence of aqueous NaOH ? (Meghalaya S.B. 2015)
- What happens when phenol is oxidised? (Uttarakhand S.B. 2015)
- Write the structural formula of propane-1,2,3-triol. (Assam S.B. 2016)
- Name the products obtained when anisole is treated with HI .
- Why is special care taken to distil old samples of ether?
- Name the products obtained when anisole is treated with a mixture of conc. HNO_3 and conc. H_2SO_4 .
- Complete the reaction.



- Give the IUPAC name of the following compound $\text{CH}_3-\text{C}(\text{Br})=\text{CH}-\text{CH}_2\text{OH}$. (D.S.B. 2009)



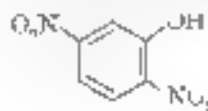
- Draw the structural formula of 3-methylpropan-2-ol. molecule. (L.S.B. 2012)
- Draw the structure of hex-1-en-3-ol compound. (D.S.B. 2012, Tripura S.B. 2016)
- Name the compound according to IUPAC rule.



(Assam S.B. 2012)

- Which of the following isomers is more volatile o-nitrophenol or p-nitrophenol? (D.S.B. 2014)

- Write the IUPAC name of



(D.S.B. 2015)

- Complete the reaction.



(Hr. S.B. 2016)

19. Give the IUPAC name of



(Jammu S.B. 2018)

20. Give the IUPAC name of



(Jammu S.B. 2018)

CBSE QUESTIONS

21. Write the structure of the molecule of a compound whose IUPAC name is 1-Phenylpropan-2-ol

(A.I.S.B. 2016)

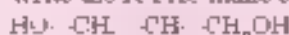
22. How would you convert ethanol to ether?

(A.I.S.B. 2012 H.P.S.B. 2014)

23. Why is
- \pm
- butan-2-ol optically inactive?

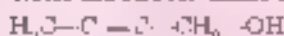
(D.S.B. 2013 A.I.S.B. 2015)

24. Write the IUPAC name of the given compound



(A.I.S.B. 2015)

25. Write the IUPAC name of the following compound



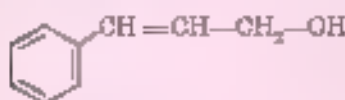
(A.I.S.B. 2017)

26. Write the IUPAC name of the following compound



(A.I.S.B. 2017)

27. Write the IUPAC name of the following compound



(A.I.S.B. 2017)

28. Write the IUPAC name of the following



(A.I.S.B. 2018)

MCQs from State Boards' Examinations

29. Dehydration of tertiary alcohols with
- Cr
- at 573 gives

- (a) Aldehydes (b) Ketones
(c) Alkenes (d) None of these (Hr. S.B. 2013)

30. Molecular formula of ethers is

- (a) $\text{C}_n\text{H}_{2n+2}\text{O}$ (b) $\text{C}_n\text{H}_{2n}\text{O}$
(c) $\text{C}_n\text{H}_{2n+1}\text{O}$ (d) None of these

(Hr. S.B. 2014 2017)

31. Williamson's synthesis is an example of

- (a) Nucleophilic substitution reaction
(b) Nucleophilic addition
(c) Electrophilic substitution
(d) None of the above (Hr. S.B. 2014)

32. Reaction used for the preparation of ethers is

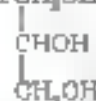
- (a) Reimer-Tiemann reaction
(b) Williamson's synthesis
(c) Wurtz reaction
(d) Cannizzaro reaction (H.P.S.B. 2014)

33. The test used to distinguish alcohols from one another is known as

- (a) Hausberg's test (b) 2, 4-DNP test
(c) Iodoform test (d) Lucas Test

(H.P.S.B. 2014)

34. The IUPAC name of
- CH_3OH
- is



- (a) Propane 1, 3-diol (b) Propane 1, 2-diol
(c) Propane 1, 2, 3-triol (d) Glycerol

(Mizoram S.B. 2015)

35. Ethers on hydrolysis give

- (a) carboxylic acid (b) alcohol
(c) ester (d) ketone
(Nagaland S.B. 2015)

36. Which of the following has highest boiling point?

- (a) Methanol (b) Ethanol
(c) Propan-1-ol (d) Butan-1-ol
(Hr. S.B. 2015)

37. Which has highest value of
- pK_a
- ?

- (a) Phenol (b) Ethanol
(c) α -Nitrophenol (d) α -Cresol (Hr. S.B. 2016)

38. Which of the following is most acidic?

- (a) Benzyl alcohol (b) Cyclohexanol
(c) Phenol (d) m -Chlorophenol
(Hr. S.B. 2017)

39. Phenols on reaction with conc.
- HNO_3
- in the presence of conc.
- H_2SO_4
- gives

- (a) α -nitrophenol (b) m -nitrophenol
(c) p -nitrophenol (d) 2,4,6-trinitrophenol
(Nagaland S.B. 2017)

40. Methanol and ethanol can be distinguished by using

- (a) Fehling's test (b) Iodoform test
(c) Tollen's test (d) Carbylamine test
(Mizoram S.B. 2017)

41. The IUPAC name of the compound



- (a) 3-Chloro-2,4-dimethyl- n -pentyl alcohol
(b) 2-Chloro-3,4-dimethylpentan-5-ol
(c) 4-Chloro-2,3-dimethylpentan-1-ol
(d) 2,3-Dimethyl-4-chloropentanol-1-ol (Mizoram S.B. 2017)

- 42.
- $\text{CH}_3\text{CH}_2\text{OH} \xrightarrow[413\text{ K}]{\text{conc. H}_2\text{SO}_4} \text{A'}$
- A' will be:

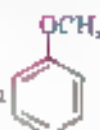
- (a) ${}^t\text{C}_4\text{H}_9$ (b) ${}^n\text{C}_4\text{H}_9$
(c) $\text{C}_4\text{H}_9\text{O}$ (d) $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$
(Hr. S.B. 2018)

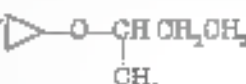
43. Which is weakest acid in the following?

- (a) H_2O (b) ${}^t\text{C}_4\text{H}_9\text{OH}$
(c) $\text{CH}_3\text{CH}_2\text{OH}$ (d) CH_3COOH
(Hr. S.B. 2018)

44. Williamson synthesis is used to prepare

- (a) Alcohol (b) Amine
(c) Ketone (d) Ether
(Hr. S.B. 2018)

45. In the reaction  + HI $\xrightarrow{373\text{ K}}$ A + B
A and B are
(a) $\text{C}_6\text{H}_5\text{I}$, CH_3OH (b) $\text{C}_6\text{H}_5\text{OH}$, CH_3I
(c) $\text{C}_6\text{H}_5\text{CH}_2\text{OH}$, CH_3I (d) $\text{CH}_3\text{CH}_2\text{I}$, $\text{C}_6\text{H}_5\text{OH}$ (Hr S.B. 2018)

46. The IUPAC name of  is—
(a) 2-Cyclopropoxybutane
(b) 2-Propoxybutane
(c) 2-Propoxypropane
(d) 2-Methyl-2-propoxypropane (Mizoram S.B. 2018)
47. Neutral ferric chloride test can be used to distinguish between
(a) Alcohols and ethers (b) Aldehydes and ketones
(c) Amines and aldehyde (d) Phenols and alcohols (Mizoram S.B. 2018)

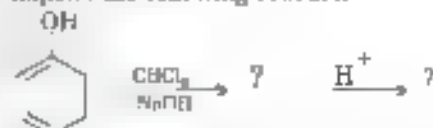
48. On reaction with aqueous bromine at room temperature phenol forms which of the following?
(a) *meta*-Bromophenol (b) 2, 6-Dibromophenol
(c) 2, 4, 6-Tribromophenol (d) 3, 5-Dibromophenol (WB S.B. 2018)

Short Answer Questions (carrying 2 or 3 marks)

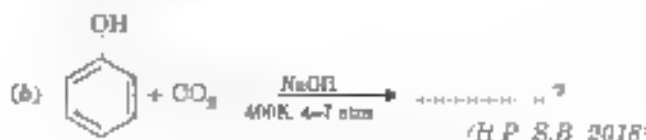
- Write the structural formulae of all the isomeric compounds that can be represented by the molecular formula $\text{C}_4\text{H}_{10}\text{O}$. Write their IUPAC names.
- How is anisole prepared? How does it react with
(a) Br_2 in CS_2
(b) HNO_3 in the presence of H_2SO_4
(c) HI at 303–403 K?
- Explain the following
(a) Phenyl methyl ether reacts with HI to give phenyl and methyl iodide and not iodobenzene and methyl alcohol.
(b) Dimethyl ether is completely soluble in water but diethyl ether is soluble in water to small extent.
(c) $\text{C}-\text{O}-\text{C}$ bond angle in ethers is higher than the $\text{H}-\text{O}-\text{H}$ bond angle in water though oxygen is sp^3 hybridized in both these cases. (Pb.S.B. 2017)
- How would you account for the following
(i) Phenol is more acidic than ethanol (Pb. S.B. 2018, Hr. S.B. 2018)
(ii) The boiling points of ethers are much lower than those of the alcohols of comparable molar masses (D.S.B. 2007, Pb.S.B. 2017, Meghalaya S.B. 2017)
(iii) Why do ethers possess dipole moment? (Pb. S.B. 2017)
- Write the equations for the reactions of phenol with the following
(i) Br_2 water
(ii) $\text{CHCl}_3 + \text{NaOH}$
(iii) $\text{Na}_2\text{Cr}_2\text{O}_7 + \text{Conc. H}_2\text{SO}_4$ (Hr. S.B. 2018)
- Explain the mechanism of the following reactions
(i) Acid catalysed dehydration of an alcohol forming an alkene. (D.S.B. 2006, Mizoram S.B. 2017, 2018)

- Acid catalysed hydration of an alkene forming alcohol (D.S.B. 2009)
- Illustrate the following reactions giving a chemical equation for each
(i) Kolbe's reaction (D.S.B. 2010)
(ii) Williamson's synthesis. (D.S.B. 2010, Pb. S.B. 2017)
(iii) Friedel Crafts alkylation. (Pb. S.B. 2017)
 - How can you distinguish primary, secondary and tertiary alcohols by Lucas test? (H.P.S.B. 2011, 2017)
 - (a) Convert phenol into salicylic acid. (H.P.S.B. 2018)
(b) How can you distinguish primary, secondary and tertiary alcohols by Lucas test? (H.P.S.B. 2018, Jamuna S.B. 2018)
(c) Explain Williamson synthesis. (H.P.S.B. 2018)
(d) Dimethyl ether has less boiling point than ethyl alcohol. Explain. (H.P.S.B. 2018)
 - How will you obtain
(i) Picric acid (3, 4, 6-trinitrophenol) from phenol
(ii) 2-Methyl propene from 2-methyl propanol (D.S.B. 2011)

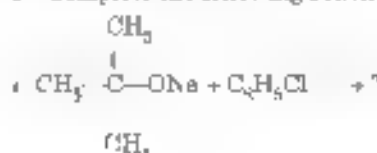
11. (a) Complete the following reaction

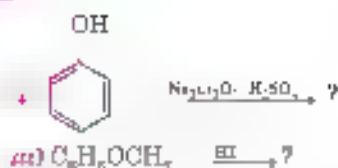


- (b) Alcohols are comparatively more soluble in water than hydrocarbons of comparable molecular mass. (H.P.S.B. 2012, 2016, Meghalaya S.B. 2018)
12. (a) Name the reagents and give the equation for the preparation of 2-methyl-2-methoxypropane [$\text{CH}_3-\text{C}(\text{OCH}_3)(\text{CH}_3)_2$] by Williamson's method
(b) Explain why 4-nitrophenol is more acidic than 4-methoxyphenol. (Meghalaya S.B. 2013)
13. Complete the following reactions



14. Give an example for each of the following
(i) Kolbe reaction
(ii) Reimer-Tiemann reaction (Jharkhand S.B. 2013)
15. How will you convert
(i) Propene to propan-2-ol
(ii) Phenol to 2, 4, 6-tribromophenol? (D.S.B. 2013)
16. How will you convert the following
(i) Propan-2-ol to propanone
(ii) Phenol to 2, 4, 6-tribromophenol (D.S.B. 2013)
17. (a) How will you distinguish between propan-1-ol and 2-methylpropan-2-ol?
(b) Complete the following reactions





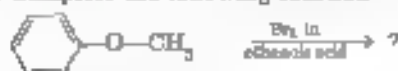
Meghalaya S.B. 2019

18. (a) Write a chemical test to distinguish between phenol and benzoic acid.
 (b) How will you convert phenol to benzoic acid?
 (c) How will you convert sodium phenoxide to salicylic acid? (Pb S.B. 2015)
19. Give a method of preparation of 3° alcohol.
 (a) State the mechanism of the reaction



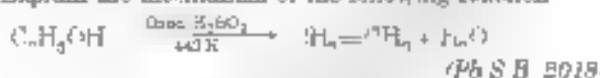
H

(a) Complete the following reaction



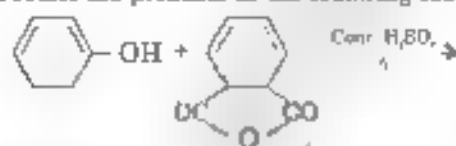
- (b) Explain why alkoxy group (-OR) is ortho, para-directing and activates the aromatic ring towards electrophilic substitution. (Assam S.B. 2018)
20. (a) Arrange the following compounds in increasing order of acidity
 H_2O , $\text{C}_2\text{H}_5\text{OH}$ and phenol
 (b) How can the following pair be chemically distinguished?
 Phenol and ethyl alcohol
 OR
 (a) Write the structural formulae of all the possible ethers having the molecular formula $\text{C}_4\text{H}_{10}\text{O}$ and give their IUPAC names.
 (b) Why are boiling points of ethers lower than those of alcohols? (Meghalaya S.B. 2015)
21. What are primary, secondary and tertiary alcohols? What happens when primary, secondary and tertiary alcohols are oxidized using acidified KMnO_4 ? (Uttarakhand S.B. 2015)

22. (a) Why are phenols acidic in nature?
 (b) Explain the mechanism of the following reaction:



(Pb S.B. 2018)

(c) Predict the products in the following reaction.



(Pb S.B. 2018)

23. (a) How will you prepare phenol from chlorobenzene? Write equation.
 (b) Explain why the boiling points of ethers are much lower than those of alcohols of comparable molecular masses.
 (c) How is picric acid prepared? (H.P.S.B. 2015)
24. (a) Why are phenols more acidic than alcohols? What happens when phenol is treated with excess of aqueous bromine solution? (Nagaland S.B. 2018)
 (b) Write the mechanism of acid catalyzed dehydration of ethanol to ethene.
 (c) Between phenol and alcohol which is more acidic? Why? (Karnataka S.B. 2018)

25. (a) Discuss dehydrogenation of primary and secondary alcohol.
 (b) What happens when vapours of primary, secondary and tertiary alcohols are passed over heated copper at 573 K? (Hr S.B. 2016)

26. Explain the following behaviours

- (i) Alcohols are more soluble in water than the hydrocarbons of comparable molecular masses.
 (ii) Ortho-nitrophenol is more acidic than ortho-methoxyphenol.
 (iii) Cumene is a better starting material for the preparation of phenol. (CBSE Sample Paper 2017-18)

27. How do you convert the following

- (i) Phenol to anisole
 (ii) Propan-2-ol to 2-methylpropan-2-ol
 (iii) Aniline to phenol

OR

- (a) Write the mechanism of the following reaction
 $2 \text{CH}_3\text{CH}_2\text{OH} \xrightarrow{\text{H}^+} \text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_3$
 (b) Write the equation involved in the acetylation of salicylic acid. (D.S.B. 2015)

28. (a) Give a simple chemical test to distinguish between primary, secondary and tertiary alcohols.

H.P.S.B. 2015



Give structures of A and B products. (Hr.S.B. 2016)

- (c) Compare the acidic strength of primary, secondary and tertiary alcohols. (Nagaland S.B. 2015)

29. (a) How would you convert the following

- (i) Phenol to benzene
 (ii) Phenol to benzoquinone
 (iii) Propan-2-ol to propan-2-ol
 (b) How will you distinguish between benzyl alcohol and phenol?

OR

(a) Complete the following reaction:



- (b) How do you overcome the immiscibility of ethoxyethane in water?
 (c) Among HI and HBr which is a better reagent for cleavage of ether? (Hr S.B. 2018)

30. (a) Give the chemical equation for the reaction of ethanol with conc. H_2SO_4 at 440 K.

- (b) Convert phenol to salicylic acid (2-hydroxybenzoic acid).

Meghalaya S.B. 2018

31. (i) Why have ethers low boiling points than isomeric alcohols?
 (ii) Give the position isomer of $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$ Butan-1-ol. (Pb S.B. 2016)

32. (a) Differentiate between primary, secondary and tertiary alcohols by chemical test. (Pb.S.B. 2018)

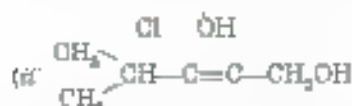
- (b) Why are primary alcohols more acidic than secondary alcohols?

- (c) Discuss the dehydrogenation of primary, secondary and tertiary alcohols. (Pb.S.B. 2016)

33. Ethers possess a dipole moment even if the alkyl radicals in the molecule are identical. Explain.

- (a) Give the position isomer of $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$ Propan-1-ol. (Pb S.B. 2016)

34. (a) Write the IUPAC names of the following compounds:



(b) Starting from phenol how phenolphthalein is obtained? *J K S.B. 2016.*

35. (a) Give one example of each of the following reactions:

(i) Reimer-Tiemann reaction

(ii) Williamson's synthesis

(b) Convert Propanone to 2-methylpropanol

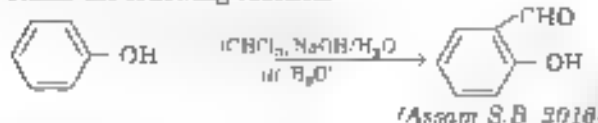
Tripura S.B. 2016.

36. An organic compound $\text{A}(\text{C}_4\text{H}_8\text{O})$ reacts with sodium to form compound B and hydrogen gas. When heated with conc. H_2SO_4 at 415K, A produces $\text{C}(\text{C}_4\text{H}_6\text{O})$. C on treatment with conc. HI at 373K forms D. C is also obtained when B is heated with D. Identify A, B, C and D and write chemical equations for the formation of B from A and formation of C from B and D. *Kolkata S.B. 2016.*

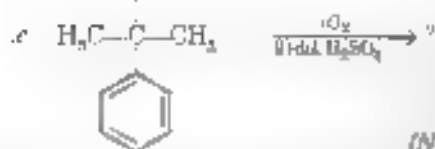
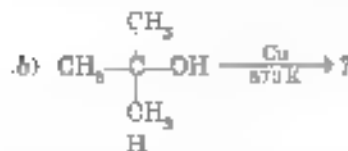
37. (a) Explain why alcohols are more soluble in water compared to ether?

(b) What happens when phenol is heated with Zn dust? Give equation.

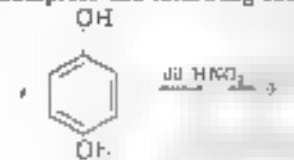
(c) Name the following reaction:



38. Complete the following reactions:

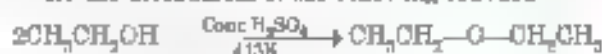


39. (a) Complete the following reactions:

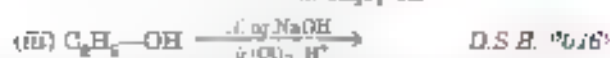
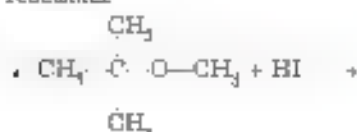


(b) Explain Williamson synthesis. *(Kerala S.B. 2016)*

40. (a) Write the mechanism of the following reaction:



(b) Write the main product(s) in each of the following reactions:



41. (a) Phenol has higher boiling point than toluene. Why?
(b) Why are alcohols easily protonated but phenols are not protonated? *Pb S.B. 2017*

42. (a) Discuss the acidic nature of phenols. *(Hr S.B. 2017)*

(b) Name any two tests to distinguish alcohol from phenol.

(c) p-Nitrophenol is more acidic than phenol. Explain why? *Hr S.B. 2017*

43. How do primary, secondary and tertiary alcohols differ towards oxidation reaction? *(Nagaland S.B. 2017)*

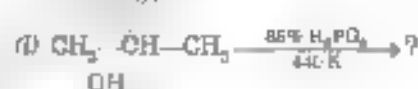
44. (a) Give reason why phenols are acidic in nature.

(b) Give one general method of preparation of 3° alcohol. Give equation.

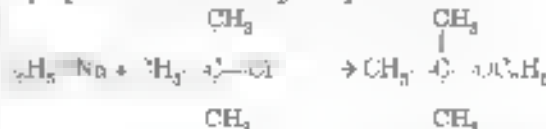
(c) Complete the following reaction and name the product.



45. (a) Complete the following reactions:



(b) The following is not an appropriate reaction for the preparation of tert-butyl ethyl ether:



Write a suitable reaction for the preparation of tert-butyl ethyl ether. *(Meghalaya S.B. 2017)*

46. (a) Arrange the following compounds in the order of increasing boiling points:

Ethanol, Propan-1-ol, Butan-1-ol, Butan-2-ol.

(b) In the lab. students were asked to carry out the reaction between phenol and conc. HNO_3 . But one student, A, carried out the reaction between phenol and dil. HNO_3 . Do you think that the student A got the same result as others. Substantiate with suitable explanations. [Also write the chemical equations wherever necessary.] *(Kerala S.B. 2017)*

47. Lucas test is used to identify primary, secondary and tertiary alcohols.

(a) Explain the process.

(b) Name the reagents used in the test.

Kerala S.B. 2018

CBSE QUESTIONS

48. Explain:

(i) Ortho-nitrophenol is more acidic than ortho-methoxyphenol.

(ii) -OH group attached to the carbon of benzene ring activates it towards electrophilic substitution.

A.I.S.B. 2005

49. How would you convert the following:

(i) Phenol to benzoquinone

(ii) Propanone to 2-methyl propan-2-ol

(iii) Propene to propan-2-ol

A.I.S.B. 2010

50. How would you obtain the following

- Benzoquinone from phenol
- 2-Methylpropan-2-ol from methyl magnesium bromide
- Propan-2-ol from propene. (A.I.S.B. 2011)

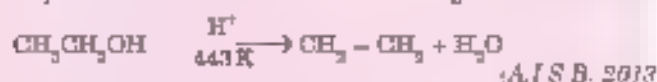
51. Explain the mechanism of acid catalysed hydration of an alkene to form corresponding alcohol. (A.I.S.B. 2012)

52. Explain the following

Alcohols are more soluble in water than hydrocarbons of comparable molecular masses.

- Ortho nitrophenol is more acidic than ortho methoxyphenol (A.I.S.B. 2012)

53. Explain the mechanism of the following reaction



54. Write the mechanism of the following reaction



55. Give reasons for the following

- o*-nitrophenol is more acidic than *o*-methoxyphenol
- Butan-1-ol has a higher boiling point than diethyl ether
- $\text{CH}_3\text{CH}_2\text{C}(\text{O})\text{CH}_3$ on reaction with HI gives $\text{CH}_3\text{CH}_2\text{C}(\text{O})\text{I}$ and $\text{CH}_3\text{CH}_2\text{OH}$ as the main products and not $(\text{CH}_3\text{CH}_2\text{C}(\text{O})\text{OH})$ and $\text{CH}_3\text{CH}_2\text{I}$ (A.I.S.B. 2015)

56. Write the chemical equations involved in the following reactions

- Kolbe's reaction
- Friedel Crafts acetylation of anisole

Or

How do you convert

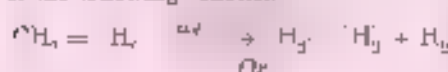
- Phenol to toluene
- Formaldehyde to ethanol (A.I.S.B. 2016)

57. Give reasons for the following

- Protonation of phenols is difficult whereas ethanol easily undergoes protonation
- Boiling point of ethanol is higher than that of dimethyl ether
- Anisole on reaction with HI gives phenol and CH_3I as main products and not *o*-iodoanisole and CH_3OH (A.I.S.B. 2016)

58. (a) Arrange the following compounds in the increasing order of their acid strength
p-cresol, *p*-nitrophenol, phenol

- Write the mechanism using curved arrow notation of the following reaction



Or

Write the structures of the products when Butan-2-ol reacts with the following

- CrO_3
- SOCl_2 (A.I.S.B. 2017)

Or

- Discuss the dehydrogenation of primary alcohols

- Write the following reactions

- Diethyl ether with HI
- Phenol with benzene diazonium chloride
- Alcohol with SOCl_2 (Ph. S.B. 2012)

2. (a) Discuss the acidic dehydration of primary alcohols at 443 K.

- Write Reimer-Tiemann reaction
- Write two uses of ethanol

Or

- Why are ethers relatively inert compounds?

- Write the following reactions

- Diethyl ether with Cl_2
- Phenol with zinc dust
- Alcohol with PCl_5 (Ph. S.B. 2012)

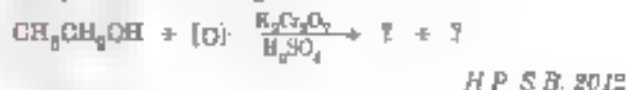
3. Account for the following

- Out of phenol and benzene which is more easily nitrated and why?

- How will you convert benzene diazonium chloride to phenol?

- Friedel Crafts alkylation reaction.

Complete the following reaction



4. (a) Write short notes on

- Wurtz reaction
- Finkelstein reaction
- Seytzeff's rule

- Complete the following reactions



5. (a) Write IUPAC names of all the possible isomers with the molecular formula $\text{C}_5\text{H}_{10}\text{O}$

- Phenol is usually manufactured from cumene. Write the structure of cumene

- Primary, secondary and tertiary alcohols can be distinguished by Lucas test.

What is Lucas reagent?

- Write the observation for primary secondary and tertiary alcohols in Lucas test (Kerala S.B. 2013)

6. (a) What happens when phenol is treated with

- CO_2 at 1-7 atm pressure

- Br_2/CS_2

- CHCl_3 , NaOH at 340 K

Give reactions also.

- How will you distinguish between isopropyl alcohol and ethyl alcohol (Hr. S.B. 2013)

7. (a) Explain the mechanism of dehydration of alcohols to give alkenes.

- What happens when phenol is treated with

- dil. HNO_3
- Conc. HNO_3

- How will you prepare phenol from

- Halobenzenes
- Diazonium salts

- Cumene

(Hr. S.B. 2015)

8. (a) How will you prepare the following compounds using Grignard reagent

- Primary alcohol
- Secondary alcohol?

- How will you distinguish primary and secondary alcohols using Lucas test?

Long Answer Questions – (Carrying 5 marks)

1. (a) Discuss the acidic dehydration of primary alcohols at 443 K.

- Write Kolbe reaction of phenol

- Write two uses of methanol

- c) Write the correct pair of reactants for the preparation of *t*-butyl ethyl ether by Williamson synthesis.

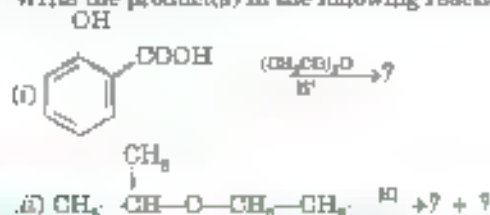
Kerala S.B. 2014

9. Give chemical reactions when  is reacted with

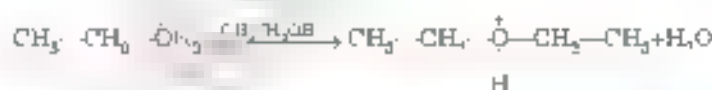
- (i) Zn (ii) Conc. HNO_3
 (iii) Bromine water (iv) CHCl_3 + eq. NaOH
 or

Explain with examples the preparation of alcohols by using hydroboration oxidation of aldehydes and ketones. Also give chemical reactions involved. (Hr. S.B. 2015)

10. a) Write the product(s) in the following reactions



- b) $\text{CH}_3-\text{CH}=\text{CH}-\text{CH}_2-\text{OH}$ $\xrightarrow{\text{KMnO}_4}$?
 (b) Give simple chemical tests to distinguish between the following pairs of compounds
 i) Ethanol and Phenol
 ii) Propanal and 2-methylpropan-2-ol
 Or
 a. Write the formula of reagents used in the following reactions
 i) Bromination of phenol to 2,4,6-tribromophenol
 (ii) Hydroboration of propene and then oxidation to propanol.
 (b) Arrange the following compound groups in the increasing order of their property indicated
 (i) *p*-nitrophenol, ethanol, phenol (acidic character)
 (ii) Propanol, Propane, Propanal (boiling point)
 (c) Write the mechanism (using curved arrow notation) of the following reaction

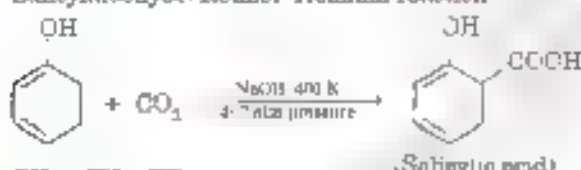
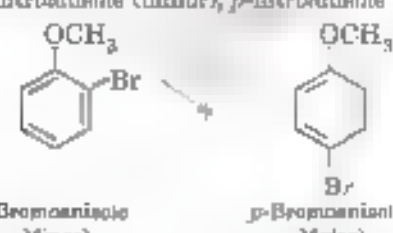
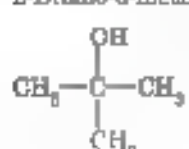


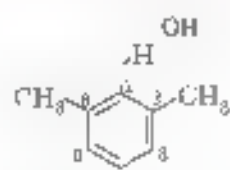
D.S.B. 2017

Hints & Answers

for Revision Exercises

Very Short Answer Questions

- But-2-ene, $\text{CH}_3\text{CH}=\text{CHCH}_3$
- $1^\circ + 2^\circ + 3^\circ$
- 2-Methylpropene
- Saccharaldehyde, Reimer-Tiemann reaction

- $\text{CH}_3-\text{CH}=\text{CH}_2$
- $\text{CH}_3-\text{CH}(\text{OH})-\text{CH}_2\text{OH}$
- Phenol and tetramethane
- The old samples of ethers may contain some peroxides because of their oxidation in the presence of light. The peroxides of ethers may decompose violently on heating resulting serious accidents.
- o*-nitroanisole (minor), *p*-nitroanisole (major)

- 2-Bromo-3-methylbut-2-en-1-ol


- $\text{CH}_3=\text{CH}-\text{CH}(\text{CH}_3)-\text{CH}_2\text{CH}_2\text{CH}_3$
- 5-Bromocyclohexanol
- p*-Nitrophenol
- 2-*o*-Dinitrophenol
- $\text{C}_2\text{H}_5\text{OC}_2\text{H}_5 + 2\text{HI} \xrightarrow{273\text{K}} 2\text{C}_2\text{H}_5\text{I} + \text{H}_2\text{O}$
- 2-Ethoxypropane
- 1,1-Dimethoxyethane
- $\text{C}_6\text{H}_5\text{CH}_2-\text{CH}=\text{CH}_2$
- 
- (\pm)-Butan-2-ol represents racemic mixture of (+)-butan-2-ol and (-)-butan-2-ol, which rotates the plane polarized light in different directions but to equal extent. Therefore, (\pm)-butan-2-ol is optically inactive.
- 2-Methylpropan-1,3-diol
- 2-Bromo-3-methylbut-2-en-1-ol
- 2-Methoxy-2-methylpropane
- 3-Phenylprop-2-en-1-ol
- 3,3-Dimethylpentan-2-ol
- (c) 30. (b) 31. (a) 32. (b) 33. (d)
- (c) 35. (b) 36. (d) 37. (b) 38. (d)
- (d) 40. (b) 41. (c) 42. (c) 43. (a)
- (d) 45. (b) 46. (c) 47. (d) 48. (c)

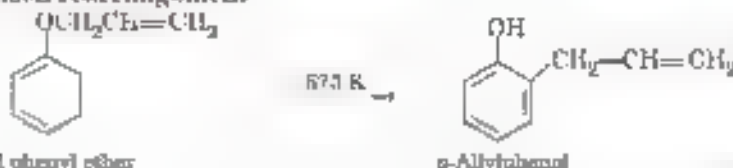
Competition File

Additional Useful Information and Objective Questions

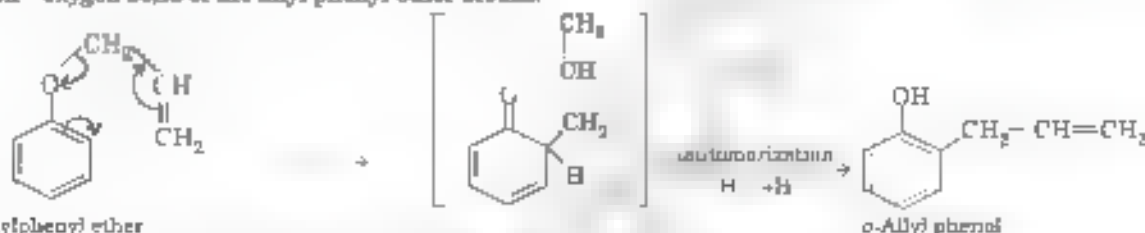
ADDITIONAL USEFUL INFORMATION

► SOME MORE NAME REACTIONS

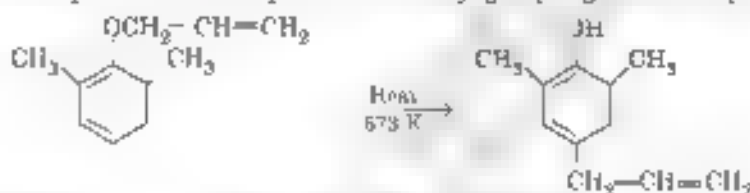
Claisen rearrangement. When allyl phenyl ethers are heated to 673 K, they undergo an intramolecular rearrangement in which the allyl group migrates from the phenolic oxygen atom to ortho position of the benzene ring forming *o*-allyl phenol. This reaction is called **Claisen rearrangement**.



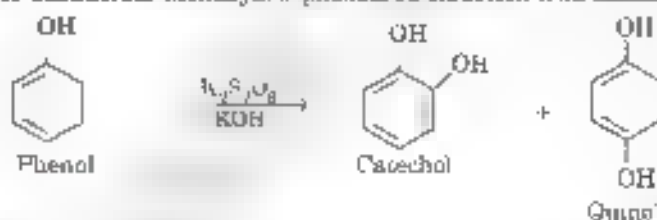
In this reaction, the bond between C—O of the allyl group and the *ortho* position of the benzene ring forms at the same time so that the carbon—oxygen bond of the allyl phenyl ether breaks.



If both the *ortho* positions are occupied, then the allyl group migrates to the *para* position.

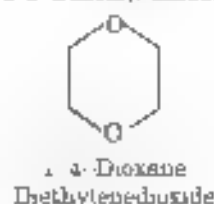
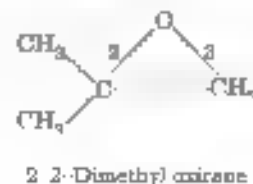
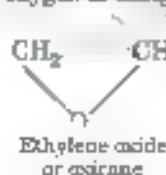


Kilb persulphate oxidation. Monohydric phenols on oxidation with alkaline potassium persulphate give dihydric phenols.



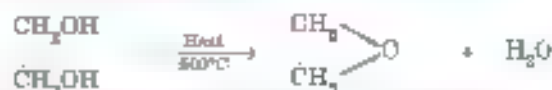
► CYCLIC ETHERS

In addition to normal ethers, some cyclic ethers are also important. Cyclic ethers are named as oxides or epoxy compounds. The three and four membered cyclic ethers are named as **oxiranes** and **oxitanes** respectively. In cyclic ethers, numbering is done in such a way that oxygen is assigned number 1. Some common examples are:

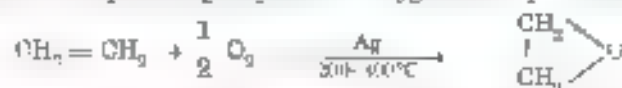


Competition File

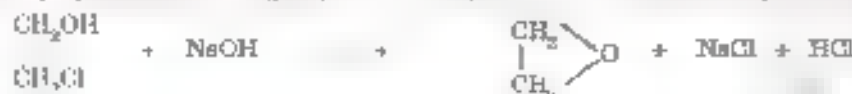
Epoxides are prepared by heating ethylene glycol at 500°C



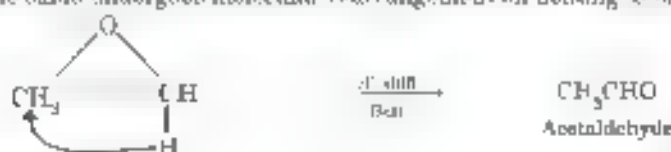
It is manufactured by heating ethylene and oxygen under pressure in the presence of silver catalyst at 200–400°C



It may also be prepared by distilling ethylene chlorohydrin with concentrated aqueous solution of NaOH .



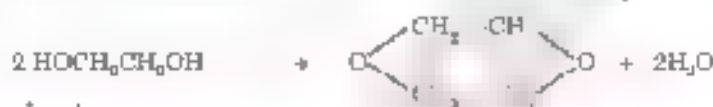
Ethylene oxide undergoes molecular rearrangement on heating to form acetaldehyde.



The substituted epoxides are reduced to alcohols with LiAlH_4 .



Dioxane is manufactured by distilling ethylene glycol with furan and H₂SO₄.



It is a very useful solvent

OBJECTIVE TYPE QUESTIONS

Multiple Choice Questions

M. C. Q.

A / Top 100 MULTIPLE CHOICE QUESTIONS
with only one correct answer

Alcohol

- A1.** When ketones are treated with Grignard reagent followed by hydrolysis with dilute acid, the product is:
- a) Primary alcohol (b) Secondary alcohol
c) Tertiary alcohol d) Alkene
- A2.** Propene on hydroboration oxidation produces
- a) Propan-1-ol (b) Propan-2-ol
c) Propane-1, 3-diol (d) Propane-1, 2-diol

- A3.** The product of acid-catalysed hydration of 2-phenylpropene gives
- (a) 2-phenylpropan-2-ol (b) 1-phenylpropan-2-ol
(c) 2-phenylpropan-1-ol (d) 3-phenylpropan-1-ol
- A4.** Which one of the following compounds would not be easily oxidised by $K_2Cr_2O_7$ and sulphuric acid?
- (a) CH_3CH_2OH (b) $(CH_3)_2CHOH$
(c) $(CH_3)_3COH$ (d) CH_3CHO
- A5.** Which of the following alcohols is most reactive with HCl in the presence of $ZnCl_2$?



Competition File



A6. Isopropyl alcohol is oxidised with $\text{K}_2\text{Cr}_2\text{O}_7$ and H_2SO_4 to give

- a) CH_3CHO b) CH_3COCH_3
c) $\text{CH}_3\text{CH}_2\text{CH}_2\text{COOH}$ d) $\text{CH}_3\text{CH}=\text{CH}_2$

A7. An alcohol of molecular formula $\text{C}_5\text{H}_{11}\text{OH}$ on dehydration gives an alkene, which on oxidation yields a mixture of ketone and an acid. The alcohol is

- a) $\text{CH}_3\text{CH}_2\text{CH}(\text{OH})\text{CH}_2\text{CH}_3$
b) $\text{CH}_3\text{CHCH}_2\text{CH}_2\text{CH}_3$

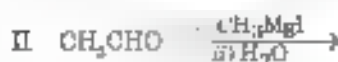
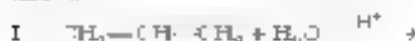


- c) $(\text{CH}_3)_2\text{CHCH}(\text{OH})\text{CH}_3$
d) $(\text{CH}_3)_2\text{CCH}_2\text{OH}$

A8. Ethanol on warming with conc. H_2SO_4 at 413 K gives

- a) ethene
b) diethyl ether
c) dimethyl ether
d) ethyl hydrogen sulphate

A9. Which one/ones of the following reactions will give propan-2-ol? Choose the right answer from (a), (b), (c), and (d)



- a) I and II b) II and III
c) III and I d) II and IV

A10. How many optically active stereoisomers are possible for butane-2, 3-diol?

- a) 1 b) 2
c) 3 d) 4

A11. 1-propanol and 2-propanol can be best distinguished by

- a) oxidation with alkaline KMnO_4 followed by reaction with Fehling solution
b) oxidation with acidic dichromate followed by reaction with Fehling solution
c) oxidation by heating with copper followed by reaction with Fehling solution
d) oxidation with conc. H_2SO_4 followed by reaction with Fehling solution

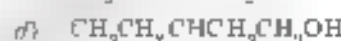
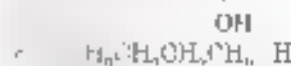
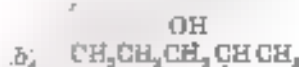
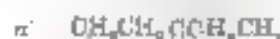
A12. During dehydration of alcohols to alkenes by heating with conc. H_2SO_4 , the initial step is

- (a) formation of an ester
(b) protonation of alcohol molecule
(c) formation of carbocation
(d) elimination of water

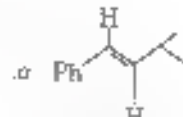
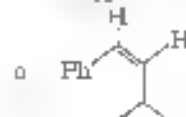
A13. Which of the following will not form a yellow precipitate on heating with an alkaline solution of iodine?

- a) $\text{CH}_3\text{CH}_2\text{CH}(\text{OH})\text{CH}_3$ b) CH_3OH
c) $\text{CH}_3\text{CH}_2\text{OH}$ d) $\text{CH}_3\text{CH}(\text{OH})\text{CH}_3$

A14. Among the following compounds which can be dehydrated very easily is



A15. The product P in the following reaction is



Phenols

A16. Phenol is more acidic than ethyl alcohol because

- (a) phenoxide ion is more resonance stabilised than phenol
(b) there is more hydrogen bonding in phenol than ethyl alcohol
(c) ethoxide ion is less resonance stabilised than ethyl alcohol
(d) phenol has higher boiling point than ethyl alcohol

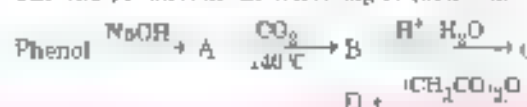
A17. Reimer-Tiemann reaction is useful for the preparation of

- a) benzaldehyde b) acetylaldehyde
c) phenol d) acetophenone

A18. Phenol on distillation with zinc dust gives

- a) benzene b) benzaldehyde
c) benzoic acid d) benzophenone

A19. The end product in the following sequence is

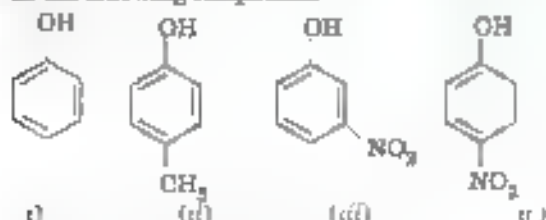


- A6.** b **A7.** c **A8.** b **A9.** a **A10.** b **A11.** c **A12.** b **A13.** b **A14.** a **A15.** b
A16. a **A17.** b **A18.** a **A19.** d

Competition File

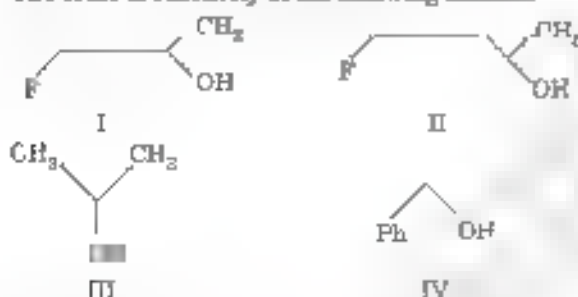
- a) Salicylic acid b) Salicylaldehyde
c) Phenyl acetate d) Aspirin
- A20.** Which of the following reagent cannot be used to distinguish between phenol and benzyl alcohol?
- a) NaOH b) NaHCO₃
c) Br₂/CCl₄ d) FeCl₃
- A21.** Phenol reacts with bromine water in CHCl₃ at low temperature to give
- a) o-Bromophenol b) o- and p-Bromophenol
c) p-Bromophenol d) 2,4,6-Tribromophenol

A22. In the following compounds



The order of acidity is

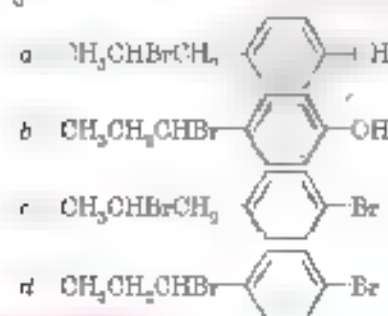
- a) iii > (iv) > i > ii
b) i > (iv) > ii > iii
c) (iii) > ii > iv > i
d) (iv) > (iii) > i > ii
- A23.** The order of reactivity of the following alcohols



towards conc. HCl is

- a) I > II > III > IV b) I > III > II > IV
c) IV > III > II > I d) IV > III > I > II

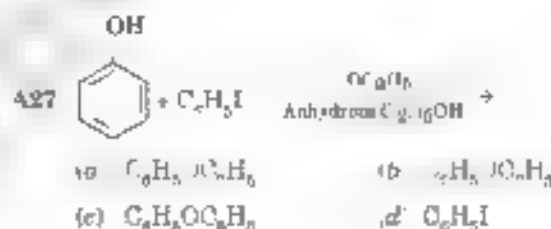
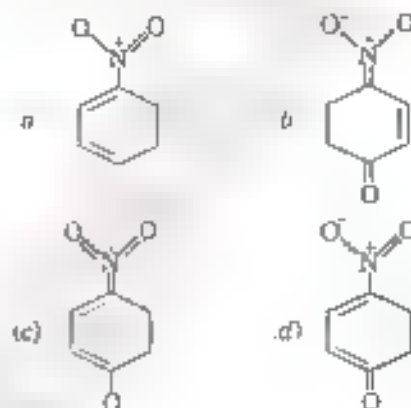
A24. The reaction of $\text{CH}_3\text{CH}=\text{CH}-\text{C}_6\text{H}_4\text{OH}$ with HBr gives



A25. Which the following will give phenol with CnO and NaOH?

- a) Salicylic acid
b) Picric acid
c) Benzoic acid
d) Amino acid

A26. The most unlikely representation of resonance structures of p-nitrophenoxide ion is



A28. When phenol is treated with CHCl_3 and NaOH, the product formed is

- a) Benzaldehyde b) Salicylaldehyde
c) Salicylic acid d) Benzoic acid

A29. When phenol is treated with conc. HNO_3 in the presence of conc. H_2SO_4 , the product is

- a) Picric acid b) p-nitrophenol
c) o-nitrophenol d) m-nitrophenol

A30. Which of the following is the strongest acid?

- a) o-methoxyphenol b) p-methoxyphenol
c) m-methoxyphenol d) phenol

Ethers

A31. Ethers are isomeric with

- a) aldehydes
b) vinyl alcohols
c) alcohols
d) ketones

Competition File

A32. Diethyl ether on treatment with excess Cl_2 gives

- a) perchlorodiethyl ether
- b) ethyl chloride
- c) ethanoyl chloride
- d) diethyl ether peroxide.

A33. Anisole reacts with HI at 373 K to give

- a) $\text{C}_6\text{H}_5\text{I} + \text{CH}_3\text{OH}$
- b) $\text{CH}_3\text{I} + \text{C}_6\text{H}_5\text{OH}$
- c) $\text{C}_6\text{H}_5\text{CH}_2\text{OH} + \text{CH}_3\text{I}$
- d) $\text{CH}_3\text{CH}_2\text{I} + \text{C}_6\text{H}_5\text{OH}$

A34. Ethers can be distinguished from alcohols by the following reaction

- a) reaction with Na
- b) reaction with PCl_5
- c) reaction with 2, 4-dinitrophenyl hydrazine
- d) none of these.

A35. In the reaction



C is

- a) Diethyl ether
- b) 1-Methoxypropane
- c) Isopropyl alcohol
- d) Propylene glycol

A36. The compound which is not isomeric with diethyl ether is

- (a) n-propyl methyl ether
- (b) 2-methyl propan-2-ol
- (c) Butanone
- (d) Butan-1-ol

A37. How many isomeric acyclic alcohols and ethers are possible for $\text{C}_4\text{H}_{10}\text{O}$?

- (a) 3
- (b) 4
- (c) 5
- (d) 7

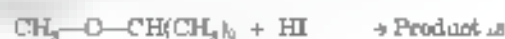
A38. Diethyl ether on heating with conc. HI gives two moles of

- (a) ethanol
- (b) iodoform
- (c) ethyl iodide
- (d) methyl iodide

A39. An ether is more volatile than alcohol having the same molecular formula. This is due to

- (a) intermolecular hydrogen bonding in alcohols
- (b) dipolar character of ethers
- (c) alcohols having resonance structures
- (d) intermolecular hydrogen bonding in ethers

A40. The major organic product in the reaction



- (a) $\text{ICH}_2\text{OCH}(\text{CH}_3)_2$
- (b) $\text{CH}_3\text{OC}(\text{CH}_3)_2$
- (c) $\text{CH}_3\text{I} + \text{CH}_3)_2\text{CHOH}$
- (d) $\text{CH}_3\text{OH} + (\text{CH}_3)_2\text{CHI}$

A32. a A33. b A34. a A35. b A36. b A37. d A38. c A39. a A40. c

B (MULTIPLE CHOICE QUESTIONS from competitive examinations AIPMT & Other State Boards' Medical Entrance

B1. Consider the following reaction



The product Z is

- (a) $\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_3$
- (b) $\text{CH}_3\text{CH}_2\text{—Si(CH}_3)_3$
- (c) $\text{CH}_3\text{CH}_2\text{OH}$
- (d) $\text{CH}_2=\text{CH}_2$

(C.B.S.E. PMT 2009)

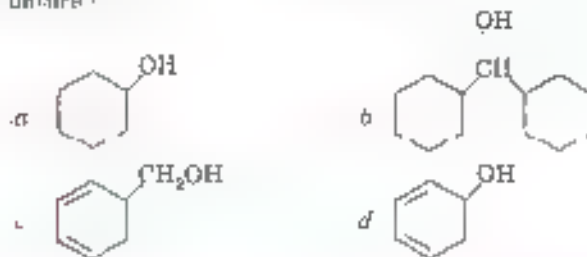
B2. Phenol $\xrightarrow{\text{alc. KOH}} \text{X} \xrightarrow[\text{Aldol}]{\text{CH}_3\text{CO}}$ Y $\xrightarrow[\text{HNO}_3]{\text{Aldol}}$ Z

The product Z is

- (a) Benzaldehyde
- (b) Benzoic acid
- (c) Benzene
- (d) Toluene

(C.B.S.E. PMT 2009)

B3. Which one of the following compounds has the most acidic nature?



(C.B.S.E. PMT 2010)

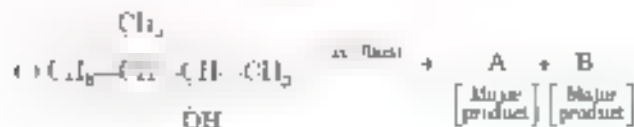
B1. c B2. b B3. d

Competition File

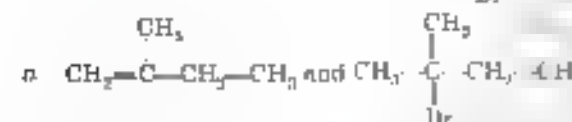
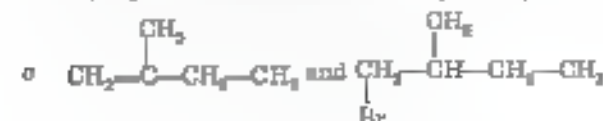
B4. Given are cyclohexanol (I), acetic acid (II), 2, 4, 6-trinitrophenol (III) and phenol (IV). In these the order of decreasing acidic character will be

- (a) II > III > IV > I (b) III > IV > II > I
(c) III > II > IV > I (d) III > II > I > IV
C.B.S.E. P.M.T. 2010

B5. In the following reactions,

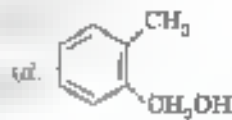
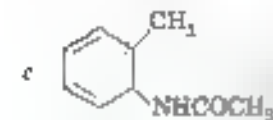
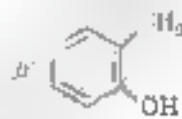
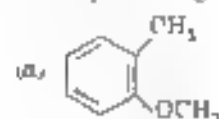


the major products (A) and (C) are respectively



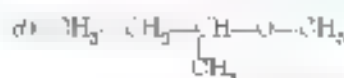
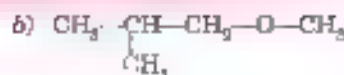
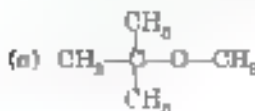
(A.I.P.M.T. 2011)

B6. Which one of the following is most reactive towards electrophilic reagent?



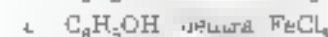
(A.I.P.M.T. 2011)

B7. Among the following ethers, which one will produce methyl alcohol on treatment with hot concentrated HI?

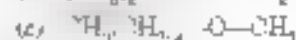


NEET 2013

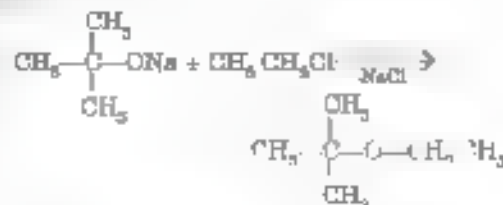
B8. Among the following sets of reactants which one produces anisole?



B9. Identify Z in the sequence of reactions.



B10. The reaction

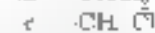


is called

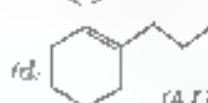
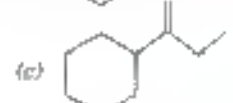
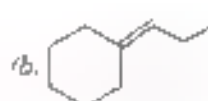
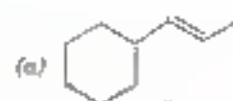
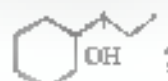


(A.I.P.M.T. 2010)

B11. Reaction of phenol with chloroform in the presence of dilute sodium hydroxide finally introduces which one of the following functional group?



B12. Which of the following is not the product of dehydration of



(A.I.P.M.T. 2015)

Competition File

B13. Which of the following reagent would distinguish *cis*-cyclopenta-1, 2-diol from *trans*-isomer?

- a) NaO_2 (b) Aluminium isopropoxide
c) Acetone (d) Ozone (NEET 2010)

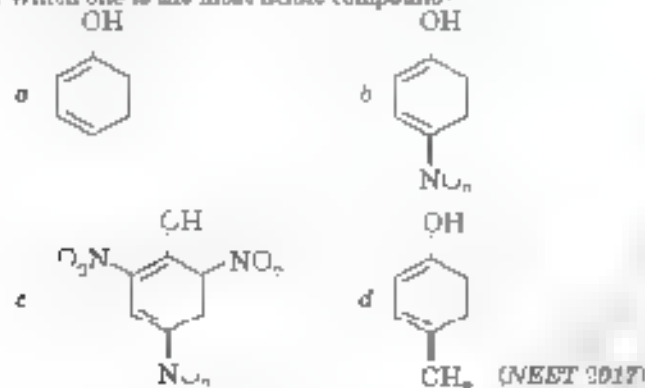
B14. The reaction,



can be classified as

- a) dehydration reaction
b) Williamson alcohol synthesis reaction
c) Williamson ether synthesis reaction
d) alcohol formation reaction (NEET 2016)

B15. Which one is the most acidic compound?



B16. The heating of phenyl methyl ether with HI produces

- a) indobenzene (b) phenol
c) benzene (d) ethyl chloride (NEET 2017)

B17. In the reaction,



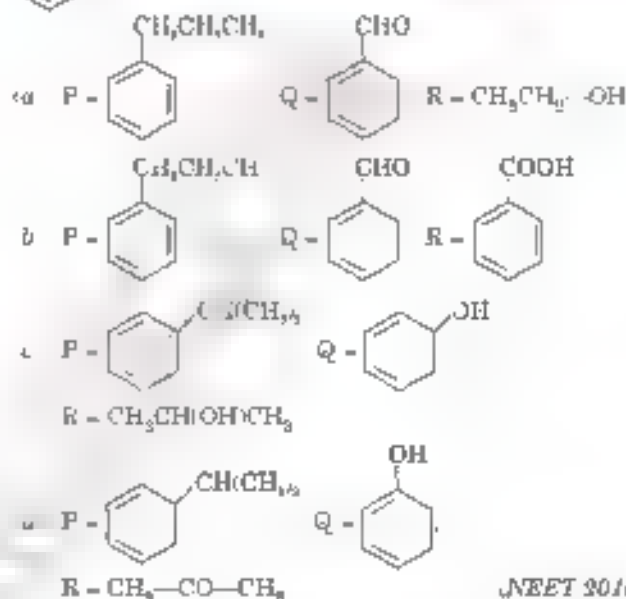
the electrophile involved is

- a) dichloromethyl cation (CHCl_2^+)
(b) formyl cation (CHO^+)
(c) dichloromethyl anion (CHCl_2^-)
(d) dichlorocarbene (CCl_2) (NEET 2018)

B18. The compound A on treatment with Na gives B and with PCl_5 gives C. B and C react together to give diethyl ether. A, B and C are in the order

- a) $\text{C}_2\text{H}_5\text{OH}$, $\text{C}_2\text{H}_5\text{I}$, $\text{C}_2\text{H}_5\text{Cl}$
b) $\text{C}_2\text{H}_5\text{OH}$, $\text{C}_2\text{H}_5\text{Cl}$, $\text{C}_2\text{H}_5\text{ONa}$
c) $\text{C}_2\text{H}_5\text{Cl}$, $\text{C}_2\text{H}_5\text{I}$, $\text{C}_2\text{H}_5\text{OH}$
d) $\text{C}_2\text{H}_5\text{OH}$, $\text{C}_2\text{H}_5\text{ONa}$, $\text{C}_2\text{H}_5\text{Cl}$ (NEET 2018)

B19. Identify the major products P, Q and R in the following sequence of reactions



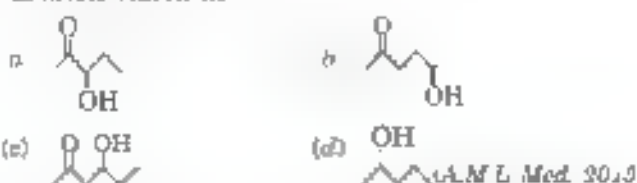
B20. The major product formed when 3,3-dimethylbutan-2-ol is heated with concentrated sulphuric acid is

- (a) 2,3-dimethyl-2-butene
(b) 3,3-dimethyl-1-butene
(c) 3,3-dimethyl-1-butene
(d) *cis*- and *trans*-isomers of 2,3-dimethyl-1-butene
(e) *cis*- and *trans*-isomers of 3,3-dimethyl-2-butene (Kerala PMT 2007)

B21. Which of the following alcohols gives the best yield of dialkyl ether on being heated with a trace of sulphuric acid?

- (a) Pentan-2-ol (b) Cyclopentanol
(c) 2-Methyl butan-2-ol (d) Propan-2-ol
(e) Pentan-1-ol (Kerala PMT 2011)

B22. Which of the following will be most readily dehydrated in acidic conditions?



B23. Which one of the following phenols has the highest pK_a value?

- (a) *o*-Nitrophenol (b) Phenol
(c) *m*-Nitrophenol (d) Picric acid
(e) *p*-resol (Kerala PMT 2014)

Competition File

JEE (Main) & Other State Boards' Engineering Entrance

B24. The major product obtained on interaction of phenol with NaOH and CO_2 is

- | | |
|--------------------|---------------------|
| (a) Benzoic acid | (b) Salicylaldehyde |
| (c) Salicylic acid | (d) Phthalic acid |

4, FEB 2009

R25. The main product of the following reaction



- $$(a) \quad \begin{array}{c} \text{C}_6\text{H}_5 \quad \text{CH}(\text{CH}_3)_2 \\ \diagdown \quad \diagup \\ \text{C} = \text{C} \\ \diagup \quad \diagdown \\ \text{H} \quad \text{H} \end{array}$$

- $$b \quad \begin{array}{c} \text{H}_6\text{C}_6\text{H}_7\text{CH}_2 \\ \text{H}_3\text{C} \end{array} \left(\begin{array}{c} \text{H}_2 \\ \text{H}_2 \end{array} \right)$$

- $$\begin{array}{c} \text{H}_2\text{C} \backslash \\ \text{C} \text{---} \text{C} \text{---} \text{H} \\ \text{H} / \end{array}$$

- $$\text{C}_6\text{H}_5\text{CH}_2 \quad \text{CH}_2$$

AIEE 2010

B26. The correct order of acidic strength of the following compounds

- | | |
|---------------------------|--------------------------|
| I Phenol | II <i>p</i> -Cresol |
| III <i>m</i> -Nitrophenol | IV <i>p</i> -Nitrophenol |

44

- a) $IV > III > I > II$ b) $II > IV > I > III$
 c) $I > II > IV > III$ d) $III > II > IV$

4. EEF cell

B27 Which of the following reagents may be used to distinguish between phenol and benzoic acid?

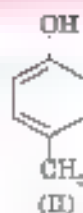
- d. Molisch reagent
e. Aqueous NaOH
f. No. test FeCl_3
g. Tollen's reagent

ALFEE 5011

B3a. *Ortho*-nitrophenol is less soluble in water than *p*- and *m*-nitrophenols because:

- (a) o-nitrophenol shows intramolecular H-bonding
(b) o-nitrophenol shows intermolecular H-bonding
(c) melting point of o-nitrophenol is lower than those of m and p-isomers
(d) o-nitrophenol is more volatile in steam than those of m- and p-isomers (AIEEE 2012)

B29. Arrange the following compounds in order of decreasing acidity



- a. $IV > III > I > II$ b. $II > IV > I > III$
c. $I > II > III > IV$ d. $III > I > II > IV$

JEE Main 2013

B80. The most suitable reagent for the conversion of $R-CH_2-OH \rightarrow R-CHO$ is

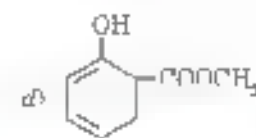
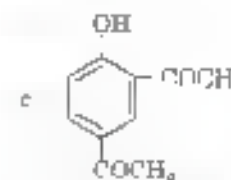
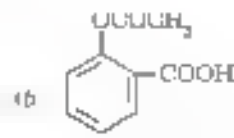
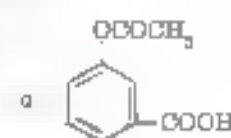
- (a) PCl_5 (Phosphorus pentachloride)
 (b) KMnO_4
 (c) $\text{K}_2\text{Cr}_2\text{O}_7$
 (d) CrO_3 /

JEE Main 2014

B31. Sodium phenoxide when heated with CO_2 under pressure at 425°C yields a product which on acetylation produces C

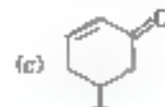
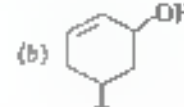
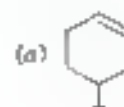
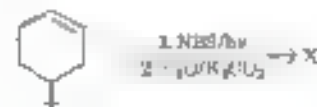


The major product C would be



JEE Main 2014

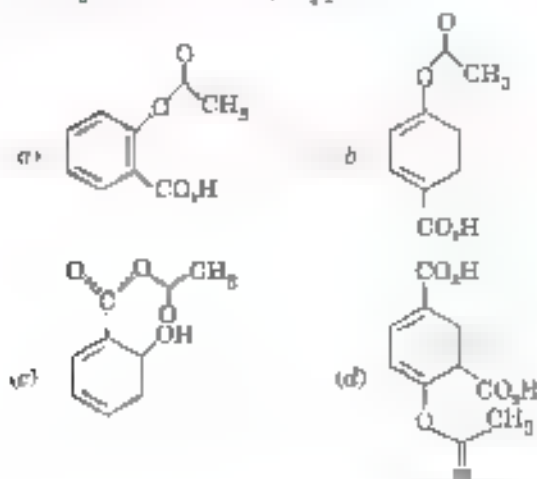
B92. The product of the numbers given below is



JEE-March 2018

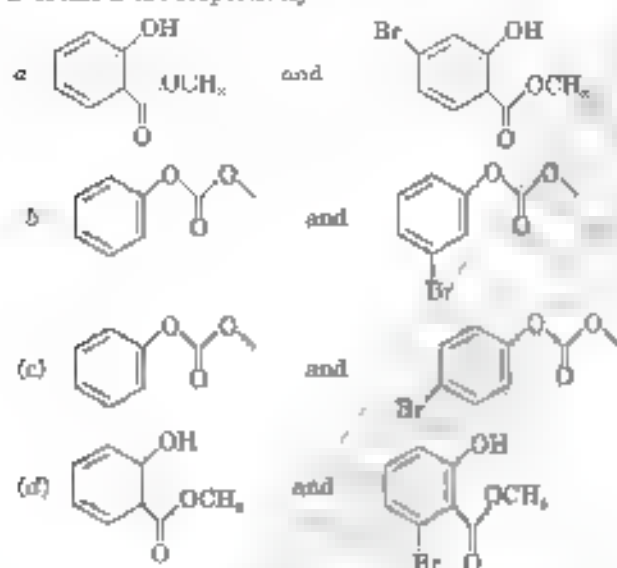
Competition File

B33. Phenol on treatment with CO_2 in the presence of NaOH followed by acidification produces compound X as the major product. X on treatment with CH_3COCl in the presence of catalytic amount of H_2SO_4 produces



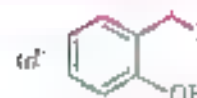
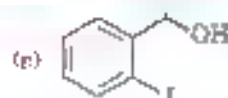
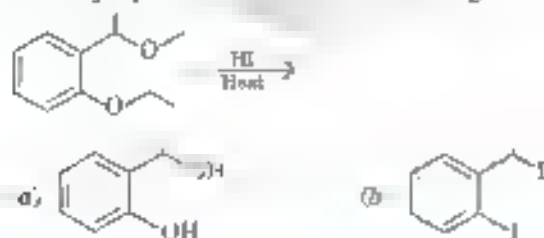
(JEE Main 2018)

B34. Phenol reacts with methyl chloroformate in the presence of NaOH to form product A. A reacts with Br_2 to form product B. A and B are respectively



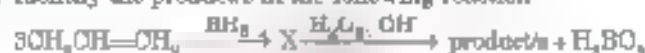
(JEE Main 2018)

B35. The major product formed in the following reaction is:



(JEE Main 2015)

B36. Identify the product/s in the following reaction

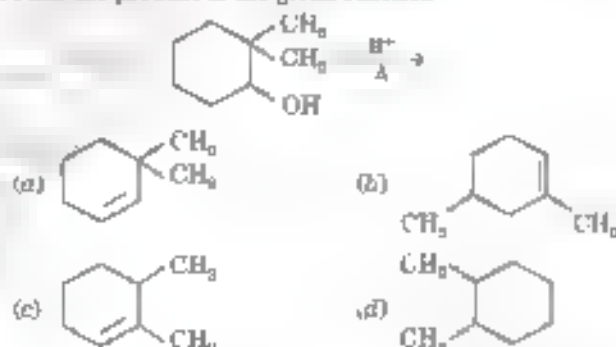


- (a) $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$ (b) $\text{CH}_3\text{CH}(\text{OH})\text{CH}_2\text{CH}_3$
 (c) $\text{CH}_3\text{CH}_2\text{CHO}$ (d) $\text{CH}_3\text{CH}_2\text{OH} + \text{CH}_3\text{OH}$
 (e) $\text{CH}_3\text{CHO} + \text{CH}_3\text{OH}$ (Kerala C.E.T. 2007)

B37. The hydroxyl compound that gives a precipitate immediately when treated with concentrated hydrochloric acid and anhydrous zinc chloride is

- (a) 3-methyl-2-butanol (b) 3-methyl-1-butanol
 (c) 1-butanol (d) 2-methyl-2-butanol
 (e) 2,3-dimethyl-1-butanol (Kerala P.E.T. 2011)

B38. Find the product of the given reaction

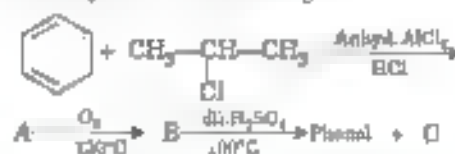


(Orissa J.E.E. 2011)

B39. An oxygen containing organic compound was found to contain 52% carbon and 18% of hydrogen. Its vapour density is 23. The compound reacts with sodium metal to liberate hydrogen. A functional isomer of this compound is

- (a) Ethanol (b) Ethanal
 (c) Methoxy methane (d) Methoxy ethane
 (Karnataka C.E.T. 2012)

B40. Identify 'C' in the following



B41. Salicylaldehyde can be prepared from phenol by

- (a) Schotten-Baumann reaction
 (b) Kolbe's reaction
 (c) Reimer-Tiemann reaction
 (d) Perkin reaction
 (e) Cannizzaro reaction (Kerala P.E.T. 2013)

Competition File

B42. The total number of cyclic structural isomers possible for compound with molecular formula $C_4H_{10}O$ is

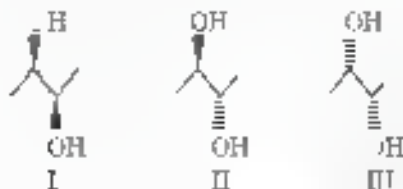
- (a) 9 (b) 7
(c) 6 (d) 8

(Kerala PET 2013, 2016)

B43. Compound 'A' of molecular formula $C_4H_{10}O$ on treatment with Lucas reagent at room temperature gives compound 'B'. When compound 'B' is heated with alcoholic KOH, it gives isobutene. Compound 'A' and 'B' are respectively

- (a) 2-methyl-2-propanol and 2-methyl-2-chloropropane
(b) 2-methyl-1-propanol and 1-chloro-2-methylpropane
(c) 2-methyl-1-propanol and 2-methyl-2-chloropropane
(d) butan-2-ol and 2-chlorobutane
(e) butan-1-ol and 1-chlorobutane (Kerala PET 2013)

B44. The correct statement regarding the following compounds is

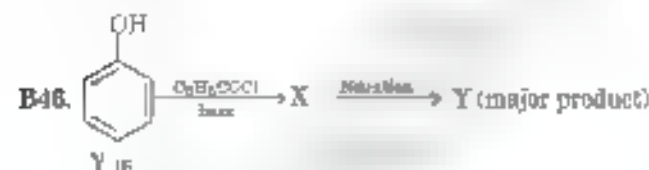


- (a) all three compounds are chiral.
(b) only I and II are chiral.
(c) I and III are diastereomers.
(d) only I and III are chiral. (WB JEE 2014)

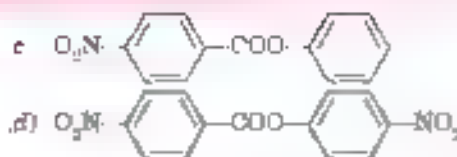
B45. Williamson's synthesis of preparing dimethyl ether is

- (a) electrophilic substitution
(b) S_N1 reaction
(c) electrophilic addition
(d) S_N2 reaction
(e) free radical substitution

(Kerala PMT 2014)



- (a)
(b)



(Karnataka CET 2014)

B47. 0.44 g of a monohydric alcohol, when added to methylmagnesium iodide in ether liberates at S.T.P., 112 cm^3 of methane. With PCl_5 the same alcohol forms a carbonyl compound that answers silver mirror test. The monohydric alcohol is

- (a) $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$
(b) $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$
(c) $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$

(d) $(\text{CH}_3)_2\text{CHCH}_2\text{CH}_2\text{OH}$ (Karnataka CET 2014)

B48. Arrange the following compounds in the increasing order of their acidic strength

- (i) m -Nitrophenol (ii) m -Chlorophenol
(iii) Phenol (iv) m -Chlorophenol
(a) $i < iv < iii < ii$ (b) $ii < iii < i < iv$
(c) $iii < ii < i < iv$ (d) $iv < iii < ii < i$

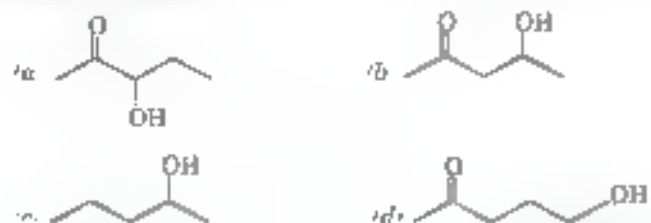
(Karnataka CET 2015)

B49. Which of the following compound would not react with Lucas reagent at room temperature?

- (a) $\text{H}_3\text{C}-\text{CH}(\text{CH}_3)-\text{CH}_2\text{OH}$ (b) $\text{C}_6\text{H}_5\text{CH}_2\text{OH}$
(c) $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$ (d) $(\text{CH}_3)_3\text{COH}$

(WB JEE 2016)

B50. Which of the following will be dehydrated most readily in alkaline medium?



(WB JEE 2016)

B51. Isopropyl methyl ether when treated with cold hydrogen iodide gives

- (a) Isopropyl iodide and methyl iodide
(b) Isopropyl alcohol and methyl iodide
(c) Isopropyl alcohol and methyl alcohol
(d) Isopropyl iodide and methyl alcohol

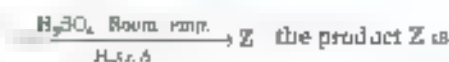
(MH CET 2016)

Answers

B42. (b) B43. (a) B44. (d) B45. (d) B46. (a) B47. (b) B48. (d) B49. (c) B50. (b) B51. (b)

Competition File

B52. In the reaction



- (a) C_2H_4 (b) $\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_3$
(c) $\text{CH}_3\text{CH}_2\text{OSO}_3\text{H}$ (d) $\text{CH}_3\text{CH}_2\text{OH}$

Karnataka CET 2016

B53. The reaction which involves dichlorocarbene as an electrophile is

- (a) Reimer-Tiemann reaction (b) Kolbe's reaction
(c) Friedel-Crafts acylation (d) Fittig's reaction

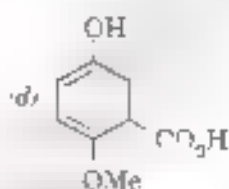
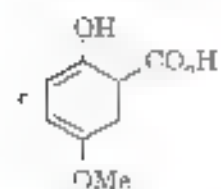
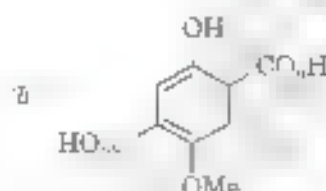
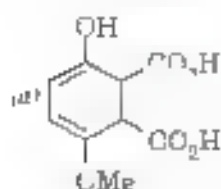
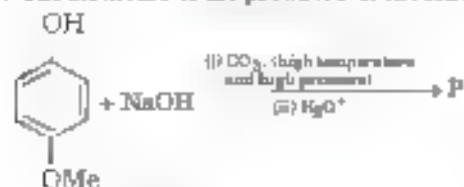
Karnataka CET 2016

B54. Ethanol is converted into ethoxyethane

- (a) by heating excess of ethanol with conc. H_2SO_4 at 140°C
(b) by heating ethanol with excess of conc. H_2SO_4 at 443 K
(c) by treating with conc. H_2SO_4 at room temperature
(d) by treating with conc. H_2SO_4 at 273 K

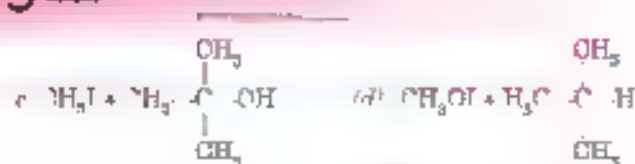
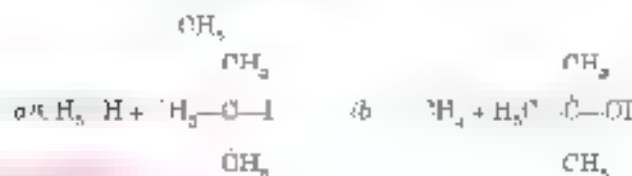
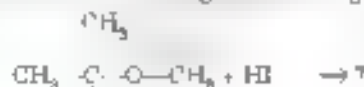
Karnataka CET 2016

B55. The structure of the product P of the following reaction is



WB JEE 2017

B56. The products formed during the following reaction are



Karnataka CET 2017

B57. Which of the following cannot be used to oxidise primary alcohols to aldehydes?

- (a) CrO_3 in anhydrous medium
(b) Pyridinium chlorochromate
(c) KMnO_4 in acidic medium
(d) Heating in presence of Cu at 573 K

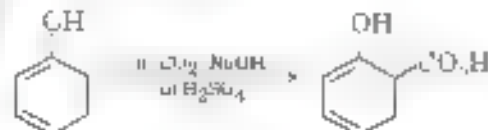
Karnataka CET 2017

B58. Which of the following orders is true regarding the acidic nature of phenols?

- (a) Phenol > o-cresol > o-nitrophenol
(b) o-cresol > phenol > o-nitrophenol
(c) Phenol < o-cresol > o-nitrophenol
(d) Phenol < o-cresol < o-nitrophenol

Karnataka CET 2017

B59. Name of the following reaction is



- (a) Reimer-Tiemann (b) Kolbe-Schmitt
(c) Cannizzaro (d) Gattermann
(e) Gattermann-Koch

(Kerala PET 2017)

B60. What product is formed when phenol is treated with CHCl_3 and NaOH ?

- (a) 1-Hydroxybenzaldehyde
(b) 2-Hydroxybenzoic acid
(c) 3-Hydroxybenzoic acid
(d) 2-Hydroxybenzaldehyde

(J K CET 2018)

B61. Methoxybenzene on treatment with HI produces

- (a) iodobenzene and methanol
(b) phenol and methyl iodide
(c) iodobenzene and methyl iodide
(d) phenol and methanol

WB JEE 2018

B62. The intramolecular hydrogen bond is present in

- (a) phenol (b) o-nitrophenol
(c) p-nitrophenol (d) p-cresol

Karnataka CET 2018

B63. Phenol can be distinguished from ethanol by the reagent

- (a) bromine water (b) sodium metal
(c) iron metal (d) chlorine water

Karnataka CET 2018

- B52. d B53. c B54. a B55. c B56. a B57. c B58. b B59. b B60. d B61. b
B62. (b) B63. a

Competition File

- B64.** When the vapours of tertiary butyl alcohol are passed through heated copper at 673 K, the product formed is
 (a) but-2-ene (b) butan-2-one
 (c) 2-methylpropene (d) butanal

Karnataka CET 2018,

- B65.** What is the increasing order of acidic strength among the following?
 i. p-methoxyphenol, ii. p-methylphenol, iii. p-nitrophenol
 (a) $i < ii < iii$ (b) $ii < i < iii$
 (c) $i < iii < ii$ (d) $ii < iii < i$

Karnataka CET 2018

- B66.** Oxidation of 1° alcohols to aldehydes is very successful for the alcohols like
 (a) pent-2-yn-1-ol (b) hexan-1-ol
 (c) n-propylalcohol (d) pentan-1-ol
 (e) octan-1-ol

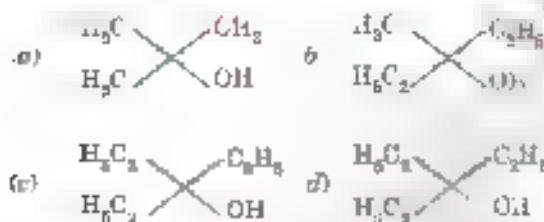
Kerala PET 2018,

- B67.** The halogen compound which will not react with phenol to give ethers is
 (a) ethyl chloride (b) methyl chloride
 (c) benzyl chloride (d) vinyl chloride
 (e) allyl chloride

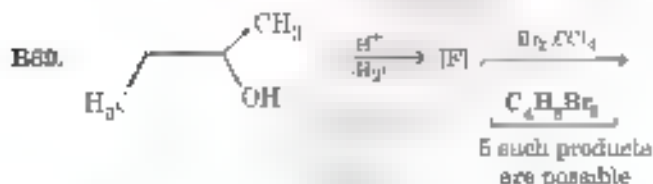
Kerala PET 2018,

JEE (Advanced) for IIT Entrance

- B68.** Ethyl ester $\xrightarrow[\text{acid}]{\text{H}_3\text{MgBr}}$ P. The product P is



IIT 2003

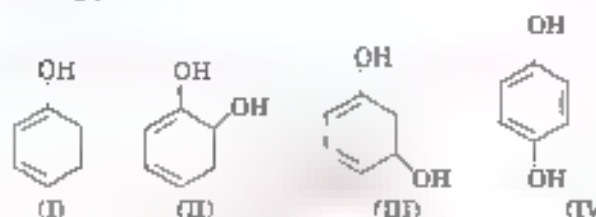


How many structures of F are possible?

- (a) 4 (b) 5
 (c) 6 (d) 8

IIT 2003

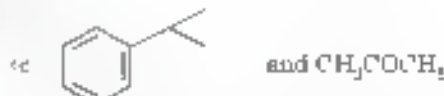
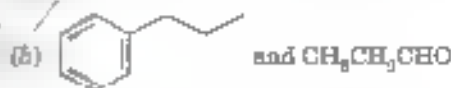
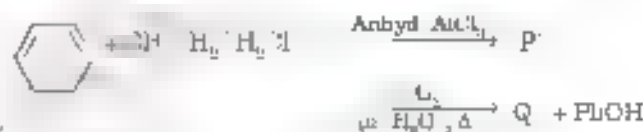
- B70.** Arrange the following compounds according to decreasing boiling points



- (a) (IV) > (III) > (II) > (I) (b) (III) > (IV) > (II) > (I)
 (c) (I) > (II) > (III) > (IV) (d) (III) > (II) > (I) > (IV)

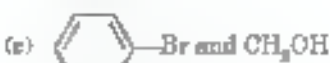
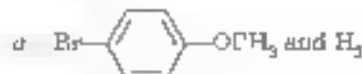
IIT 2006

- B71.** Identify the major products (P and Q) in the following reaction



IIT 2008

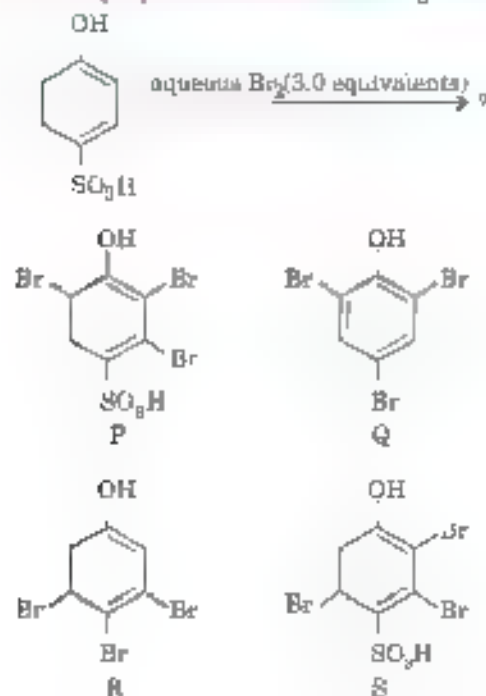
- B72.** In the reaction



IIT 2010

Competition File

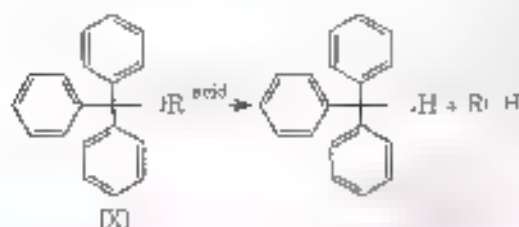
B72. The major product(s) of the following reaction is/are



$\sigma \in P$
 $\sigma \in R$

 WILEY-Blackwell 2015

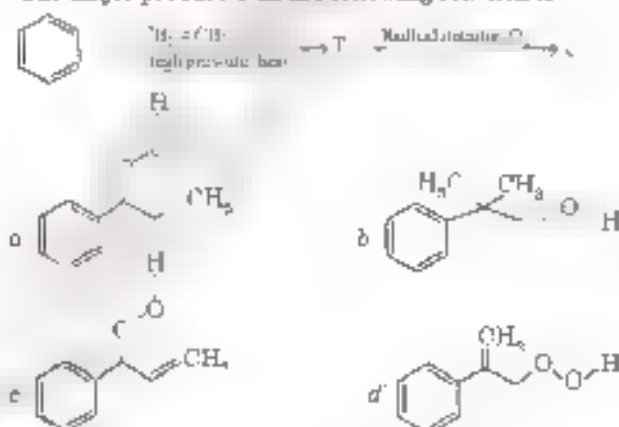
B74. The acidic hydrolysis of ether (X) shown below is fastest when



- a) one phenyl group is replaced by a methyl group
- b) one phenyl group is replaced by a para-methoxyphenyl group
- c) two phenyl groups are replaced by two para-methoxyphenyl groups
- d) no structural change is made so X

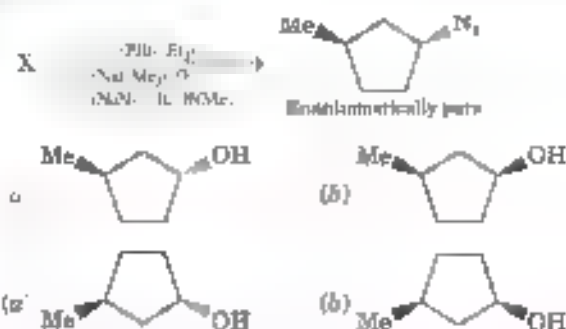
1. JEE Advanced 2014)

B75. The major product U in the following reaction is



IEEE Access 2015

B7a. In the following reaction sequence the correct structures of X and Y are



IEEE Advance 3018)

- B7E, (b) B7F, (c) B7G, (b) B7H, (b)

C { **MULTIPLE CHOICE QUESTIONS**
with more than one correct answer

Q1. Which of the following alcohols on dehydration with conc H_2SO_4 give but-2-ene ?

- a) 2-Methyl propan-2-ol
b) Butan-1-ol
c) 2-Methyl propan-1-ol
d) Butan-2-ol

Q4. Which of the following alcohols give iodoform test ?

- (a) Butan-1-ol (b) Propan-1-ol
(c) Propan-2-ol (d) Ethanol

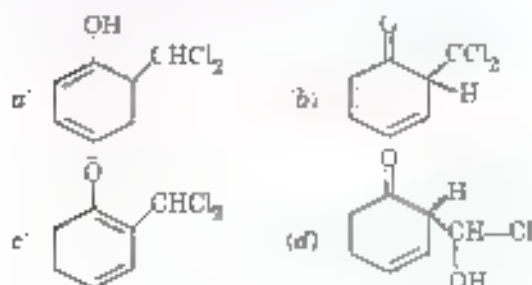
C8. Which of the following are weaker acids than phenol?

- (a) 4-Methoxy phenol (b) 3,5-dinitrophenol
(c) 4-Methyl phenol (d) 4-Nitro phenol

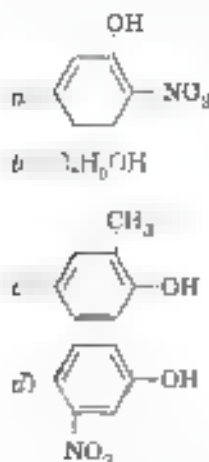
- C1, {b, d} C11, {c, d} C3, {a, c}

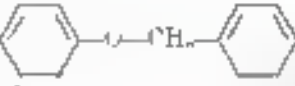
Competition File

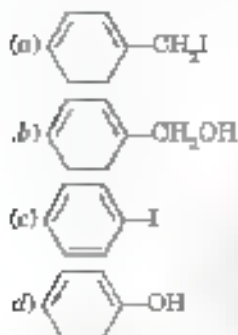
C4. When phenol is treated with CHCl_3 and NaOH followed by acidification, salicylaldehyde is formed. Which of the following species are involved in the above mentioned reaction as intermediate?



C5. Which of the following are less acidic than $\text{C}_6\text{H}_5\text{OH}$?

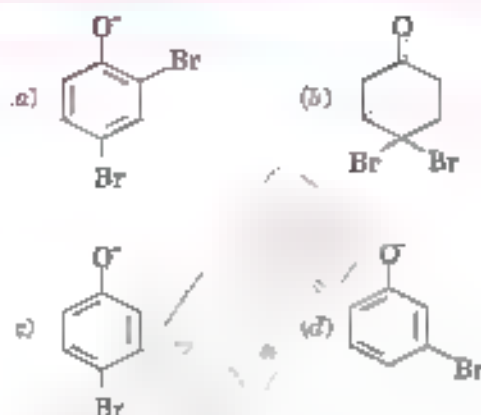
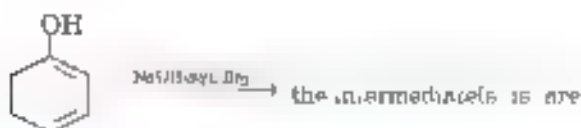


C6. The ether  when treated with HI produces



(Kerala PMT 2014)

C7. In the reaction



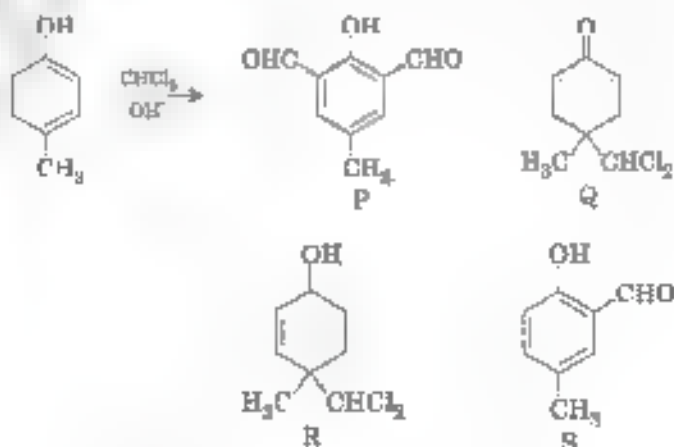
(IIT 2010)

C8. Correct statement(s) in cases of *n*-butanol and *t*-butanol is/are

- (a) both are having equal solubility in water
(b) *t*-butanol is more soluble in water than *n*-butanol
(c) boiling point of *t*-butanol is lower than *n*-butanol
(d) boiling point of *n*-butanol is lower than *t*-butanol

WB JEE Engg 2013

C9. In the following reaction, the product(s) formed is/are:



- (a) P (major) (b) Q (minor)
(c) R (minor) (d) S (major)

JEE Advance 2013

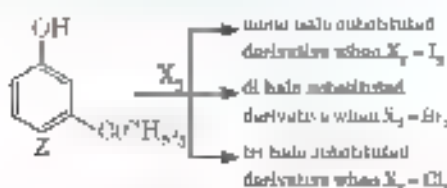
C10. The correct combination of names for isomeric alcohols with molecular formula $\text{C}_4\text{H}_{10}\text{O}$ is/are

- a) *tert*-butanol and 2-methylpropan-2-ol
b) *tert*-butanol and 1,1-dimethylethan-1-ol
c) *n*-butanol and butan-1-ol
d) *iso*-butyl alcohol and 2-methylpropan-1-ol

(JEE Advance 2014)

Competition File

- C11.** The reactivity of compound **Z** with different halogens under appropriate conditions is given below

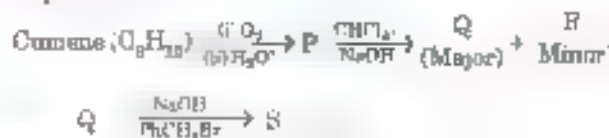


The observed pattern of electrophilic substitution can be explained by

- the steric effect of the halogen
- the steric effect of the *tert*-butyl group
- the electronic effect of the phenolic group
- the electronic effect of the *tert*-butyl group

JEE Advance 2014

- C12.** The correct statement(s) about the following reaction sequence is/are



- R is steam volatile
- Q gives dark violet colouration with 1 % aqueous FeCl_3 solution
- S gives yellow precipitate with 2,4-dinitrophenylhydrazine
- S gives dark violet colouration with 1% aqueous FeCl_3 solution

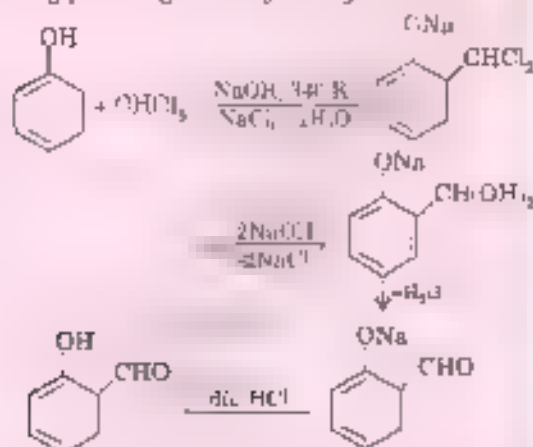
(JEE Advance 2016)

- C11.** (a, b, c) **C12.** (b, c)

D (MULTIPLE CHOICE QUESTIONS based on the given passage/comprehension

Passage-I

Phenols react with chloroform in the presence of aqueous KOH at 340 K followed by hydrolysis of the resulting product give salicylaldehyde as



Answer the following questions

- D1.** The above reaction is
 - Reimer-Tiemann reaction
 - Kolbe's reaction
 - Cannizzaro's reaction
 - Fries rearrangement
- D2.** The electrophile in this electrophilic substitution reaction is
 - COCl_2
 - COCl_2
 - CHCl_2^+
 - Cl^-
- D3.** When OCl_4 is used in place of CHCl_3 in the above reaction, the product formed is
 - 2-Acetoxybenzoic acid
 - 2-Hydroxybenzoic acid
 - 2-Carboxyphenol
 - none of these
- D4.** When the product in D3 is heated with acetic anhydride and conc. H_2SO_4 , the final product formed is used as
 - antiseptic
 - tranquilizer
 - analgesic
 - antibiotic
- D5.** When product in D3 is heated with phenol, the new product formed is called
 - oil of winter green
 - salol
 - carboxic acid
 - aspirin

- Passage I.** D1. (a), D2. (b), D3. (b), D4. (c), D5. (b)

Competition File

Passage-II

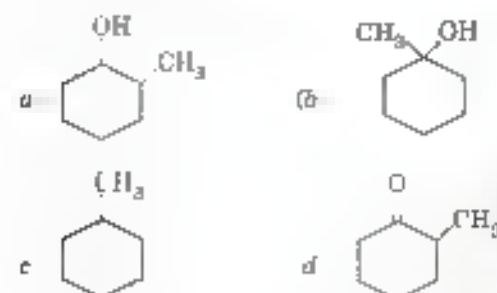
Primary and secondary alcohols are dehydrogenated by copper at 573 K to aldehydes and ketones respectively. In contrast tertiary alcohols are dehydrated to alkenes by heating with copper at 573 K. Similarly primary alcohols are easily oxidised to form first an aldehyde and then a carboxylic acid while secondary alcohols are oxidised to ketones which are further oxidised to form a mixture of acids. Tertiary alcohols are oxidised with difficulty and with strong oxidising agents in acidic medium. They form first ketones and then acids. In the case of alcohols containing carbon-carbon double bond, some oxidising agents oxidise both double bond and $-OH$ group while other reagents do not affect $C=C$ bond.

Answer the following questions :

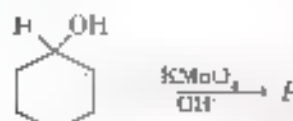
D6. In the reaction



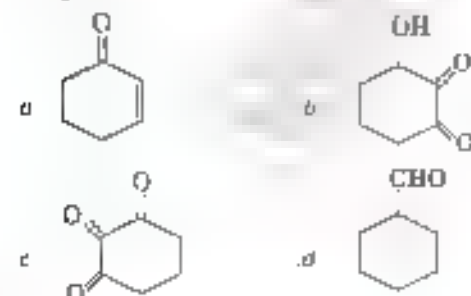
the product Y is



D7. In the reaction



The product P is



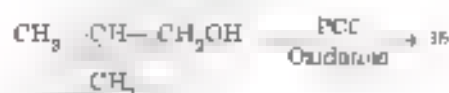
D8. Butan-2-ol on heating with Cu at 573 K gives

- (a) butane. (b) 2-butanone
(c) propanone (d) but-2-ene

D9. The reagent which oxidises 1° alcohol to aldehyde without affecting $C=C$ double bond is

- (a) CrO_3 in aqueous acetone solution
(b) aqueous $K_2Cr_2O_7$
(c) alkaline $KMnO_4$
(d) none of these

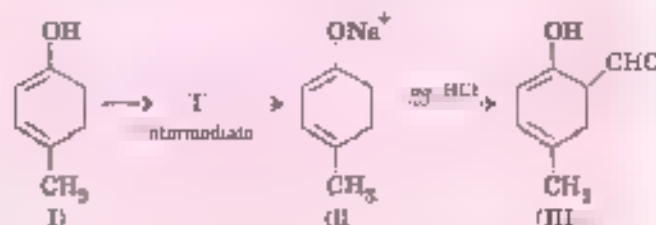
D10. The product of the reaction



- (a) 2-Methylpropanoic acid
(b) 2-Methylpropanoic acid
(c) Butanoic acid
(d) Butan-2-one

Passage-III

Reimer-Tiemann reaction introduces an aldehyde group on α -hydro aromatic ring of phenol, ortho to the hydroxyl group. This reaction involves electrophilic aromatic substitution. This is a general method of the synthesis of substituted acrylaldehydes as depicted below.



IIT 2007

Answer the following questions :

D11. Which one of the following reagents is used in the above reaction ?

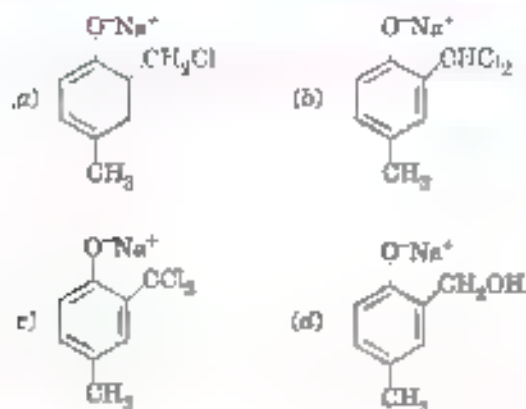
- (a) aq. $NaOH + CH_2Cl_2$
(b) aq. $NaOH + CH_2Cl_3$
(c) aq. $NaOH + CH_2Cl_4$
(d) aq. $NaOH + CCl_4$

D12. The electrophile in this reaction is

- (a) ^+HCl (b) $^+CHCl_2$
(c) $^+OCl_2$ (d) $^+CCl_2$

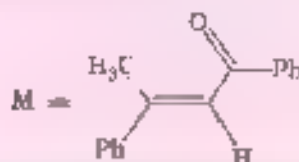
Competition File

D13. The structure of the intermediate is



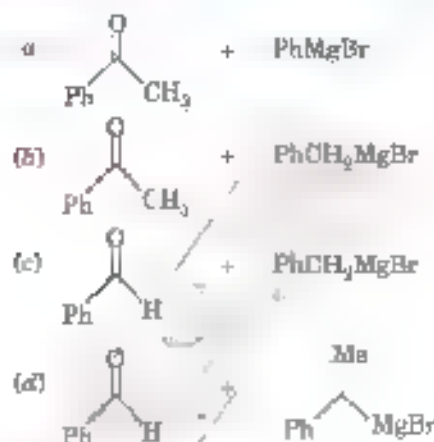
Passage-IV

A tertiary alcohol **H** upon acid catalysed dehydration gives a product **I**. Isomerisation of **I** leads to compounds **J** and **K**. Compound **J** upon reaction with HCl gives benzyl alcohol and a compound **L**, whereas **K** on reaction with KOH gives only **M**.

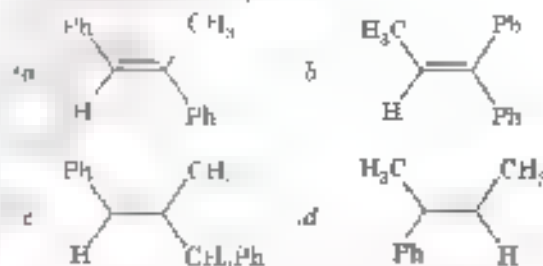


Answer the following questions

D14. Compound **H** is formed by the reaction of



D15. The structure of compound **I** is



D16. The structures of compounds **J**, **K** and **L** respectively are

- (a) PhCOCH_3 , $\text{PhCH}_2\text{COCH}_3$ and $\text{PhCH}_2\text{COO}^-\text{K}^+$
 (b) PhCHO , PhCH_2CHO and PhCOO^-K^+
 (c) PhCOCH_3 , PhCH_2CHO and $\text{CH}_3\text{COO}^-\text{K}^+$
 (d) PhCHO , PhCOCH_3 and PhCOO^-K^+ IIT 2006

Passage III. D15. b Passage IV. D14. b D15. c D16. d

Assertion Reason Type Questions

The question given below consist of an Assertion and the Reason. Use the following key to choose the appropriate answer.

- a. If both assertion and reason are CORRECT and reason is the CORRECT explanation of the assertion.
 b. If both assertion and reason are CORRECT but reason is NOT THE CORRECT explanation of the assertion.
 c. If assertion is CORRECT but reason is INCORRECT.
 d. If assertion is INCORRECT but reason is CORRECT.
 e. If both assertion and reason are INCORRECT.

1. **Assertion:** The boiling points of alcohols are higher than those of hydrocarbons of comparable molecular mass.
Reason: Alcohols show intramolecular hydrogen bonding.
 2. **Assertion:** Phenol undergoes Kolbe's reaction but ethanol does not.
Reason: Phenol is more acidic than ethanol.
 3. **Assertion:** The $\text{C}-\text{C}-\text{C}$ bond angle in ethers is higher than $\text{H}-\text{O}-\text{H}$ bond angle in water.
Reason: Oxygen in both ethers and water is sp^2 hybridized.
 4. **Assertion:** The boiling point of diethyl ether is much less than that of ethanol.
Reason: In ethanol, the molecules are associated by the formation of intermolecular hydrogen bonding whereas in diethyl ether, it is not possible.

1. (c) 2. (b) 3. (b) 4. (a)

Competition File

5. Assertion: Alcohols have higher boiling points than ethers of comparable molecular masses

Reason: Alcohols and ethers are isomeric compounds

6. Assertion: *o*- and *p*-nitrophenols can be separated by steam distillation

Reason: *o*- isomer is steam volatile due to chelation while *p*-isomer is not steam volatile due to association of molecules by intermolecular H-bonding

5. (b) 6. (a)

Matrix Match Type Questions

Each question contains statements given in two columns, which have to be matched. Statements in Column I are labelled as A, B, C and D whereas statements in Column II are labelled as *p*, *q*, *r* and *s*. Match the entries of Column I with appropriate entries of Column II. Each entry in Column I may have one or more than one correct option from Column II. The answers to these questions have to be appropriately bubbled as illustrated in the following example:

	<i>p</i>	<i>q</i>	<i>r</i>	<i>s</i>
A	<input checked="" type="radio"/>	<input checked="" type="radio"/>	<input type="radio"/>	<input type="radio"/>
B	<input checked="" type="radio"/>	<input checked="" type="radio"/>	<input type="radio"/>	<input type="radio"/>
C	<input checked="" type="radio"/>	<input checked="" type="radio"/>	<input type="radio"/>	<input type="radio"/>
D	<input checked="" type="radio"/>	<input checked="" type="radio"/>	<input type="radio"/>	<input type="radio"/>

If the correct matches are A-*q*, A-*r*, B-*p*, B-*s*, C-*r*, C-*s* and D-*q*, then the correctly bubbled matrix will look like the following:

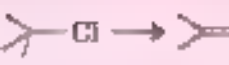
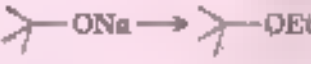


1. Match the compounds in Column I with the properties in Column II

Column I	Column II
A. butan-2-ol	<i>p</i> (free acid) than phenol
B. 3-nitrophenol	<i>q</i> gives alkene with λ_{max} 573K
C. <i>p</i> -cresol	(<i>r</i>) more acidic than ethanol
D. 2-methylpropan-2-ol	<i>s</i> gives talcous on reduction with zinc dust

(1) A - *p* B - *r* C - *p*, *s* D - *p*, *q*

Matching List Type Questions







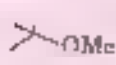



1. Match the chemical conversions in List I with the appropriate reagents in List II and select the correct answer using the code given below the lists

List I	List II
<p>P. </p> <p>Q. </p> <p>R. </p> <p>S. </p>	<p>1. (i) $\text{Hg}(\text{OAc})_2$ (ii) NaBH_4</p> <p>2. NaOEt</p> <p>3. EtBr</p> <p>4. BH_3 (ii) $\text{H}_2\text{O}_2/\text{NaOH}$</p>

	P	Q	R	S
(a)	2	3	1	4
(b)	3	2	1	4
(c)	2	3	4	1
(d)	3	2	4	1

Competition File

2. List-I contains reactions and List-II contains major products

List I	List II
P.  +  →	1. 
Q.  + HBr →	2. 
R.  + NaOMe →	3. 
S.  + MeBr →	4. 
	5. 

Match each reaction in List-I with one or more products in List-II and choose the correct option. The correct option is

- (a) P + 1, Q + 2, R + 3, S + 4
 (b) P + 1 + Q + 2, R + 4, S + 3
 (c) P + 1 + Q + 2, R + 3 + S + 4
 (d) P + 4, 5, Q + 4, R + 4, S + 3, 4

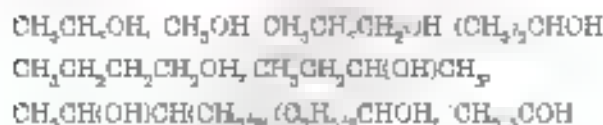
(JEE Advanced 2016)

- (1) (a) (2) (b)

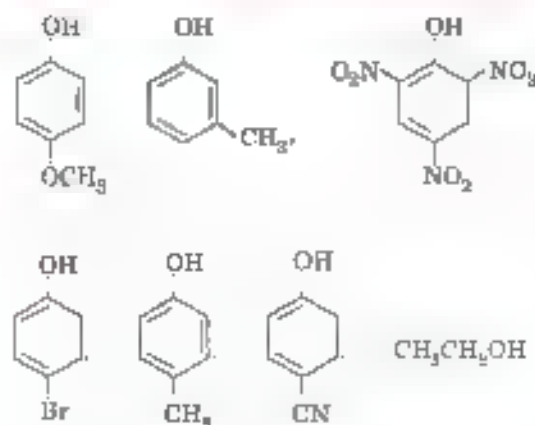
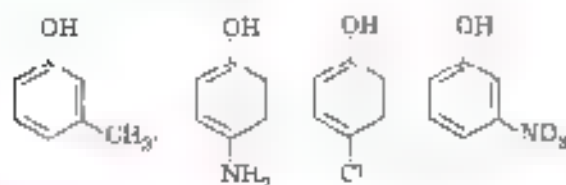
Integer Type or Numerical Value Type Questions

Integer Type: The answer to each of the following question is a single-digit-integer ranging from 0 to 9.

1. The number of alcohols giving iodoform test among the following is



2. How many of the following compounds have lower pK_a value than phenol?



3. How many of the structurally isomeric pentyl alcohols will give immediate turbidity in Lucas test?
4. The total number of structural isomers having the molecular formula $\text{C}_9\text{H}_{18}\text{O}$ is

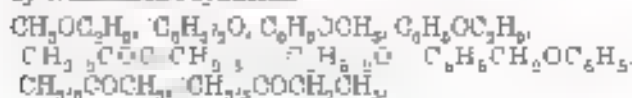
1. 4 2. 6 3. 1 4. 5

Competition File

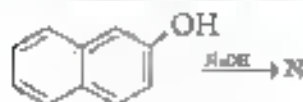
5. How many of the following compounds give 1° alcohol with Grignard reagent: H_3MgBr is

Acetaldehyde, Formaldehyde, Ethylacetate, Acetone, Oxirane, Acetyl chloride, Anhydride, Carbon dioxide, Methyl methanoate

6. How many of the following of ethers cannot be prepared by Williamson's synthesis

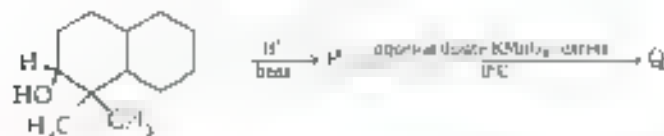


7. The number of resonance structures of **N** is



(JEE Advance 2015)

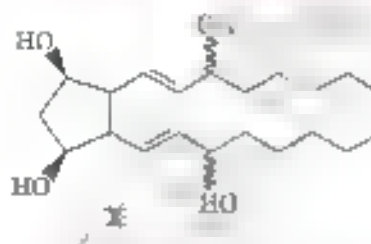
8. The number of hydroxyl groups in **Q** is



(JEE Advance 2015)

Numerical Value Type: Give the correct numerical value in decimal notation truncated/rounded off to the second decimal place

9. For the given compound **X**, the total number of optically active stereoisomers is



— This type of bond indicates that the configuration at the specific carbon and the geometry of the double bond is fixed.

~ This type of bond indicates that the configuration at the specific carbon and the geometry of the double bond is NOT fixed.

(JEE Advance 2018)

5. 2 6. 2 7. 9 8. 4 9. 7.00



NCERT

Exemplar Problems

Objective Questions

Multiple Choice Questions (Type-I)

1. Monochlorination of toluene in sunlight, followed by hydrolysis with aq. NaOH yields

(a) o-Cresol (b) m-Cresol
(c) p-Dihydroxytoluene (d) Benzyl alcohol

2. How many alcohols with molecular formula $\text{C}_4\text{H}_{10}\text{O}$ are chiral in nature?

(a) 1 (b) 2
(c) 3 (d) 4

3. What is the correct order of reactivity of alcohols in the following reaction?



(a) 1 > 2 > 3 (b) 1 < 3 > 2
(c) 3 > 1 > 2 (d) 3 > 1 < 2

4. $\text{CH}_3\text{CH}_2\text{OH}$ can be converted into CH_3CHO by

(a) catalytic hydrogenation
(b) treatment with LiAlH_4
(c) treatment with pyridinium chlorochromate
(d) treatment with KMnO_4

5. The process of converting alkyl halides into alcohols involves

(a) addition reaction
(b) substitution reaction
(c) dehydration reaction
(d) rearrangement reaction

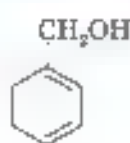
1. (d) 2. (a) 3. (c) 4. (c) 5. (b)

Competition File

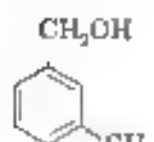
6. Which of the following compounds is aromatic alcohol?



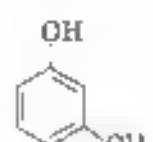
(A)



(B)



(C)



(D)

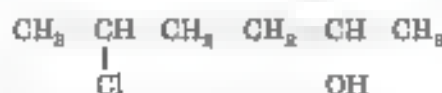
(a) A, B, C, D

(c) B, C

(b) A, D

(d) A

7. Give IUPAC name of the compound given below



(a) 2-Chloro-5-hydroxyhexane

(b) 2-Hydroxy-5-chlorohexane

(c) 5-Chlorohexan-2-ol

(d) 2-Chlorohexan-5-ol

8. IUPAC name of *m*-cresol is

(a) 3-methylphenol

(b) 3-chlorophenol

(c) 3-methoxyphenol

(d) benzene-1,3-diol

9. IUPAC name of the compound $\text{CH}_3-\text{CH}(\text{CH}_3)-\text{OCH}_3$ is

(a) 1-methoxy-1-methylethane

(b) 2-methoxy-2-methylethane

(c) 2-methoxypropane

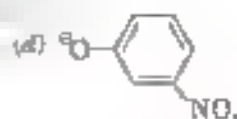
(d) isopropylmethyl ether

10. Which of the following species can act as the strongest base?

(a) ^-OH

(b) ^-OR

(c) $^-\text{OC}_6\text{H}_5$



11. Which of the following compounds will react with sodium hydroxide solution in water?

(a) $\text{C}_6\text{H}_5\text{OH}$

(b) $\text{C}_6\text{H}_5\text{CH}_2\text{OH}$

(c) $(\text{CH}_3)_3\text{COH}$

(d) O_2H_2

12. Phenol is less acidic than

(a) ethanol

(b) *p*-nitrophenol

(c) *o*-methylphenol

(d) *o*-methoxyphenol

13. Which of the following is most acidic?

(a) Benzyl alcohol

(b) Cyclohexanol

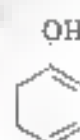
(c) Phenol

(d) *m*-Chlorophenol

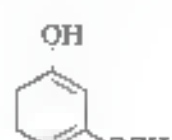
14. Mark the correct order of decreasing acid strength of the following compounds.



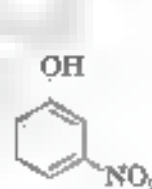
(A)



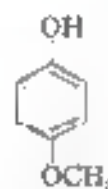
(B)



(C)



(D)



(E)

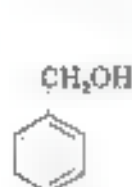
(a) $\text{E} > \text{D} > \text{B} > \text{A} > \text{C}$

(b) $\text{B} > \text{D} > \text{A} > \text{C} > \text{E}$

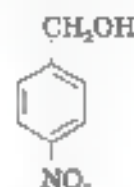
(c) $\text{D} > \text{E} > \text{C} > \text{B} > \text{A}$

(d) $\text{E} > \text{D} > \text{C} > \text{B} > \text{A}$

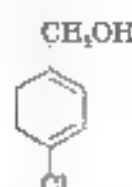
15. Mark the correct increasing order of reactivity of the following compounds with HBr/H^+



(i)



(ii)



(iii)

(a) $(i) < (ii) < (iii)$

(b) $(ii) < (i) < (iii)$

(c) $(ii) < (iii) < (i)$

(d) $(i) < (ii) < (i)$

16. Arrange the following compounds in increasing order of boiling point.

Propan-1-ol, butan-1-ol, butan-2-ol, pentan-1-ol

(a) Propan-1-ol, butan-2-ol, butan-1-ol, pentan-1-ol

(b) Propan-1-ol, butan-1-ol, butan-2-ol, pentan-1-ol

(c) Pentan-1-ol, butan-2-ol, butan-1-ol, propan-1-ol

(d) Pentan-1-ol, butan-1-ol, butan-2-ol, propan-1-ol

Competition File

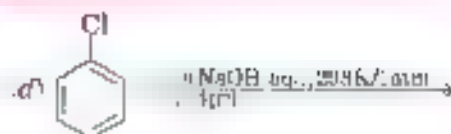
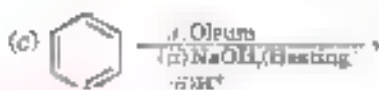
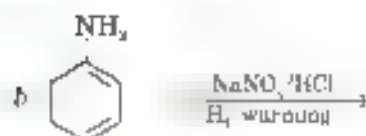
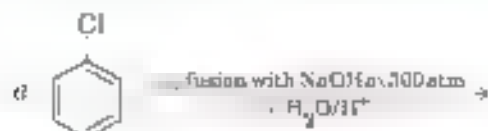
Multiple Choice Questions (Type-II)

Note In the following questions two or more options may be correct.

17. Which of the following are used to convert $RCHO$ into RCH_2OH ?

- a) H_2/Pd
- b) $LiAlH_4$
- c) $NaBH_4$
- d) Reaction with $RMgX$ followed by hydrolysis

18. Which of the following reactions will yield phenol?



19. Which of the following reagents can be used to oxidise primary alcohols to aldehydes?

- (a) CrO_3 in anhydrous medium
- (b) $KMnO_4$ in acidic medium
- (c) Pyridinium chlorochromate
- (d) Heat in the presence of Cu at $573K$

20. Phenol can be distinguished from ethanol by its reactions with

- a) Br_2/water
- b) Na
- c) Neutral $FeCl_3$
- d) All the above

21. Which of the following are benzylic alcohols?

- a) $C_6H_5-CH_2-CH_2OH$
- (b) $C_6H_5-CH_2OH$
- (c) $C_6H_5-CH(OH)-CH_3$
- a) $C_6H_5-CH_2-CH(OH)-CH_3$

17. a, b, c

18. a, b, c

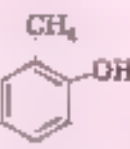
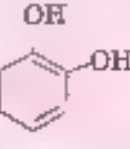
19. a, d

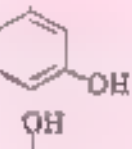
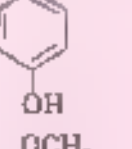
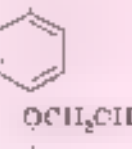

20. a, c

21. b, c

Matching Type Questions

22. Match the names of Column I and Column II in the following questions.

Column I	Column II
(a) 	(ii) Hydroquinone
b 	i. Phenetole



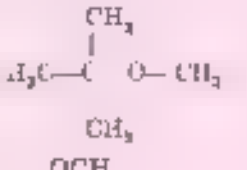


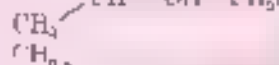
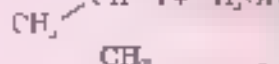
c 	(v) Catechol
(d) 	(iv) p-Cresol
e 	(vi) Quinone
f 	(vi) Resorcinol
	(vi) Anisole

22. a) (iv)

22. a) (iv); (b) (iii); c) (vi); d) (i); e) (vii); f) (v)

Competition File

22. Match the starting materials given in Column I with the products formed by these (Column II) in the reaction with HI

Column I	Column II
a. $\text{CH}_3\text{---O---CH}_3$	 + CH_3I
b. 	(i) $\text{CH}_3\text{---C---I} + \text{CH}_3\text{OH}$ CH_3
c. 	ii.  + $\text{CH}_3\text{CH}_2\text{CH}_2\text{I}$
d. 	(iv) $\text{CH}_3\text{---OH} + \text{CH}_3\text{---I}$ CH_3
	e.  + CH_3I
	vi.  + H_2OH
	(vii) $\text{CH}_3\text{---C---OH} + \text{CH}_3\text{I}$ CH_3

23. Match the items of column I with items of column II.

Column I	Column II
a. Antifreeze used in car engine	Neurax, ferric chloride
b. Solvent used in perfumes	(ii) Glycerol
c. Starting material for phoric acid	i. Methylal
d. Wood spirit	(iv) Phenol
e. Reagent used for detection of phenolic group	Ethylene glycol
f. By product of soap industry used in cosmetics	ii. Ethanol

24. Match the items of column I with items of column II.

Column I	Column II
a. Methanol	i. Conversion of phenol to o-hydroxybenzoic acid
b. Reimer-Tiemann reaction	ii. Ethyl alcohol
c. Williamson's synthesis	(iii) Conversion of phenol to salicylaldehyde
d. Oxidation of 2° alcohol to ketone	iv. Wood spirit
e. Reimer-Tiemann reaction	v. Heated copper at 573K
f. Fermentation	(vi) Reaction of alkyl halide with sodium alkoxide

22. (a) (iv); (b) (e); (c) (vi); (d) (i) 23. (a) (i); (b) (ii); (c) (iv); (d) (iii); (e) (v); (f) (vi) 24. (a) (iii); (b) (ii); (c) (vi); (d) (iv); (e) (v); (f) (i)

Assertion and Reason Type Questions

Note : In the following questions a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices

- (a) Assertion and reason both are correct and reason is correct explanation of assertion
 (b) Assertion and reason both are wrong statements
 (c) Assertion is correct statement but reason is wrong statement
 (d) Assertion is wrong statement but reason is correct statement
 (e) Both assertion and reason are correct statements but reason is not correct explanation of assertion
25. **Assertion** Addition reaction of water to but-1-ene in acidic medium yields butan-1-ol
Reason : Addition of water in acidic medium proceeds through the formation of primary carbocation.

27. **Assertion** p-nitrophenol is more acidic than phenol
Reason : Nitro group helps in the stabilisation of the phenoxide ion by dispersal of negative charge due to resonance
28. **Assertion** : IUPAC name of the compound
 $\text{CH}_3\text{---CH---O---CH}_2\text{---CH}_2\text{---CH}_3$
 CH_3
 is 2-Ethoxy-2-methylhexane
Reason In IUPAC nomenclature, ether is regarded as hydrocarbon derivative in which a hydrogen atom is replaced by ---OR or ---OAr group where R = alkyl group and Ar = aryl group
29. **Assertion** Bond angle in ethers is slightly less than the tetrahedral angle
Reason There is a repulsion between the two bulky ---R groups
30. **Assertion** Boiling points of alcohols and ethers are high
Reason They can form intermolecular hydrogen-bonding

ANSWERS

25. (b) 27. (a) 28. (d) 29. (d) 30. (b)

Competition File

21. Assertion : Like bromination of benzene, bromination of phenol is also carried out in the presence of Lewis acid.
Hanson : Lewis acid polarises the bromine molecule.

32. Assertion : *o*-Nitrophenol is less soluble in water than the *m*- and *p*-isomers.

Reason *m*- and *p*-Nitrophenols exist as associated molecules.

32. Assertion : Ethanol is a weaker acid than phenol

Reason Sodium ethoxide may be prepared by the reaction of ethanol with aqueous NaOH.

84. **Assertion** Phenol forms 2, 4, 6 tribromophenol on treatment with Br₂ in carbon disulphide at 273K.

Reason Bromine polarises in carbon disulphide

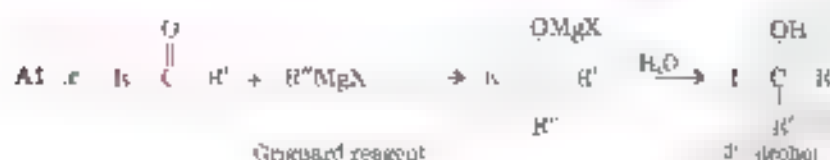
85. **Assertion** Phenols give *o*- and *p*-nitrophenol on nitration with conc. HNO_3 and H_2SO_4 mixture.

Reason : -OH group in phenol is p - p -directing.

31. *d* 32. *e* 33. *c* 34. *b* 35. *d*

Hints & Explanations for Difficult Objective Type Questions

A. mcq with only one correct answer

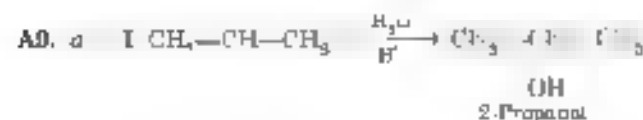
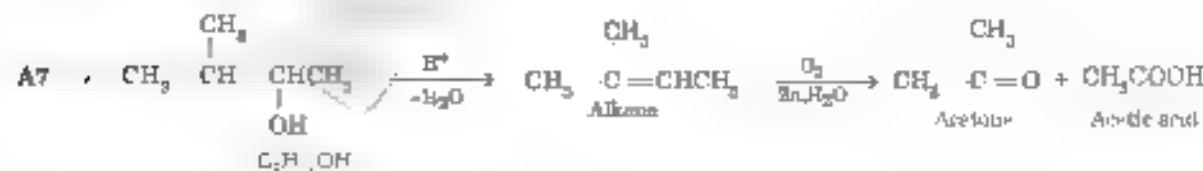
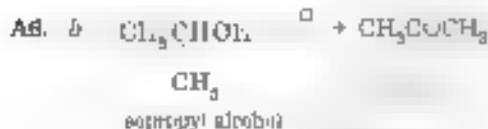


The reaction hydroboration oxidation involves addition of water molecule in accordance with Markovnikov's rule

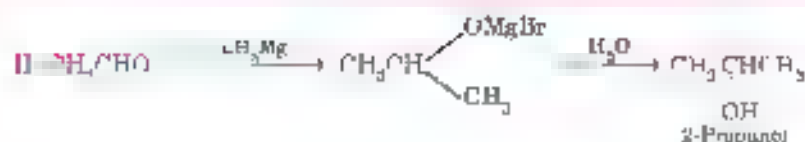


A4. c). A tertiary alcohol is very difficult to be oxidised because it does not have hydrogen on the carbon bearing -OH group.

Ans. a Tertiary alcohols have greater reactivity ($3^\circ > 2^\circ > 1^\circ$)



Competition File



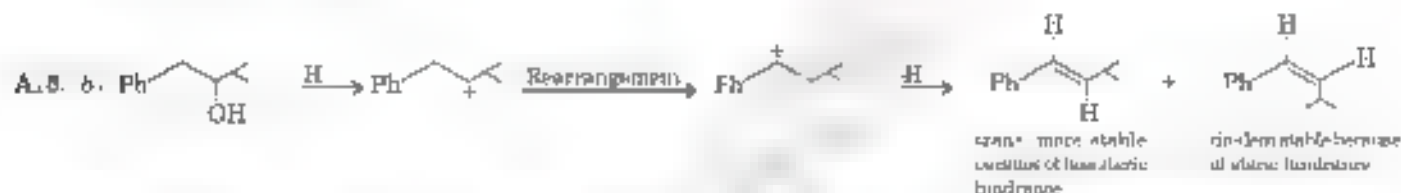
A.1. c 1-Propanol and 2-Propanol in the presence of copper (heat) undergo dehydration to give CH_3CHO and CH_3COCH_3 respectively. These can be easily distinguished by Fehling solution.

A.2. b First step is protonation of alcohol: $\text{R}^+\text{H}_2\text{C}(\text{OH})_2 + \text{H}^+ \rightarrow \text{R}^+\text{H}_2\text{C}(\text{OH})_2^+$
Protonated alcohol

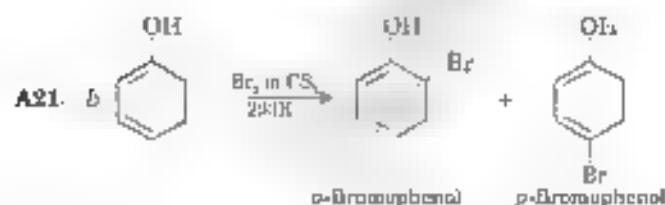
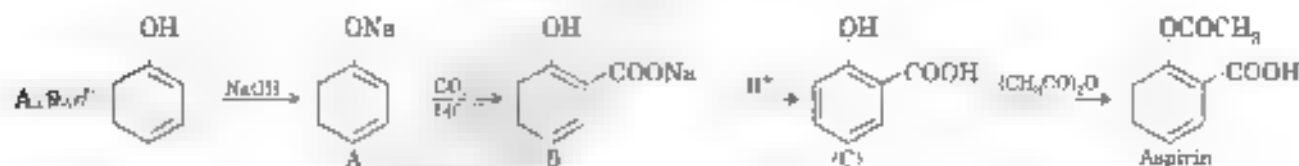
A.3. b The compound which does not contain $\text{CH}_3-\text{OH}-$ group will not give iodoform test.



A.4. a The compound $(\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_3)(\text{CH}_3\text{CH}_2\text{OH})$ produces most stable 3° carbocation and, therefore, the compound will undergo dehydration most easily.

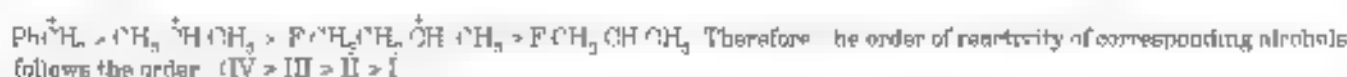


A.6. a The greater acidic character of phenol is due to more resonance stability of phenoxide ion than phenol.



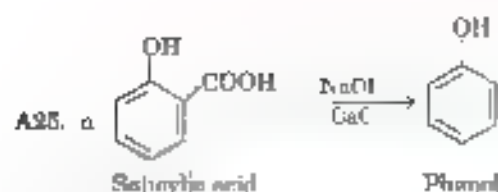
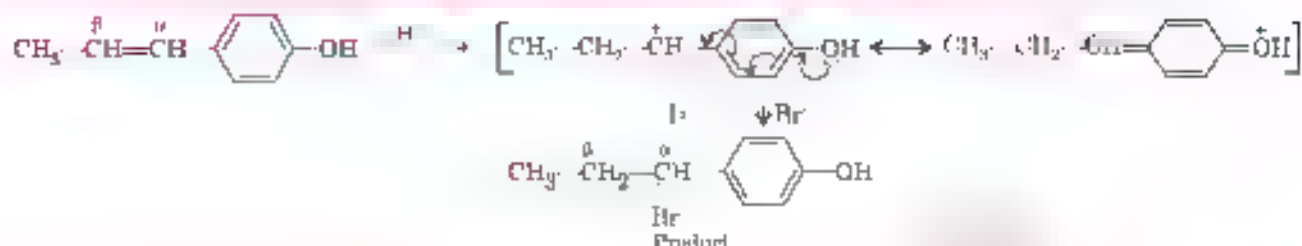
A.22. d Phenol is more acidic than cresol but less acidic than *o*-cresophenol. *p*-cresophenol is more acidic than *m*-cresophenol. Thus, the correct order is *p*-cresophenol > *m*-cresophenol > phenol > cresol.

A.23. c The order of reactivity depends upon the stability of carbocations formed. The relative stability of the carbocations follows the order:



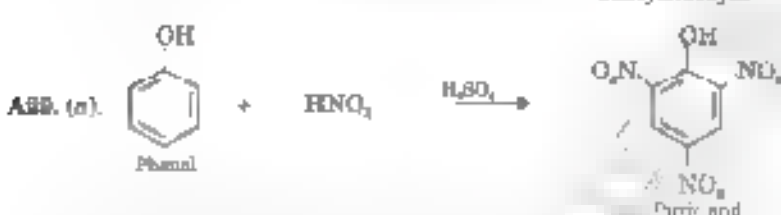
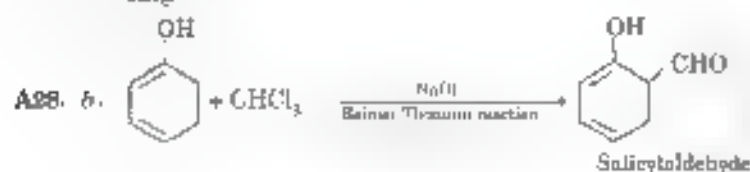
A.24. b The addition of a proton at β -carbon gives a carbocation II which is resonance stabilized because of electron donating effect of $-\text{OH}$ group. The addition of Br^- ion to the carbocation gives the main product.

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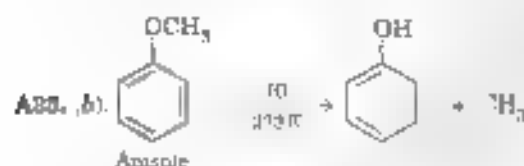
A26. c. Nitrogen cannot have 10 electrons (more than octet) in its valence shell

A27. b. $\text{C}_2\text{H}_5\text{O}^-$ is better nucleophile & attack $\text{C}_6\text{H}_5\text{I}$ than $\text{C}_6\text{H}_5\text{O}^-$. In $\text{C}_6\text{H}_5\text{O}^-$ the negative charge is delocalised over the benzene ring

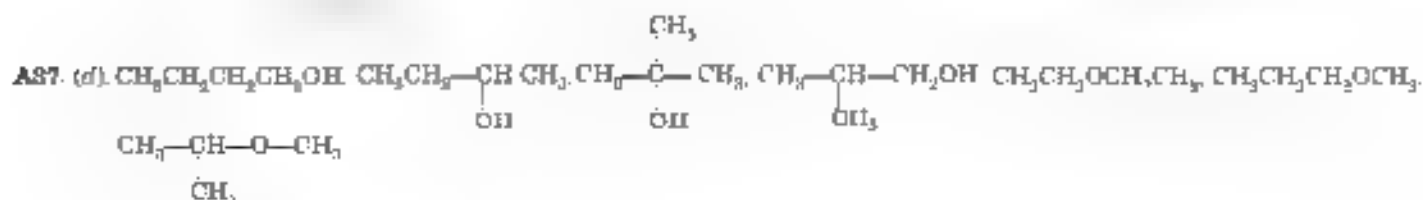


A30. c. At *m*-position, $-\text{OCH}_3$ group does not exert its +R effect. Instead, it exerts its I effect and therefore *m*-methoxyphenol is the strongest acid among phenols, *o*-, *m*- or *p*-methoxyphenol

A31. c. Ethers and alcohols are functional isomers. $\text{CH}_3\text{CH}_2\text{OH}$ or CH_3OCH_3

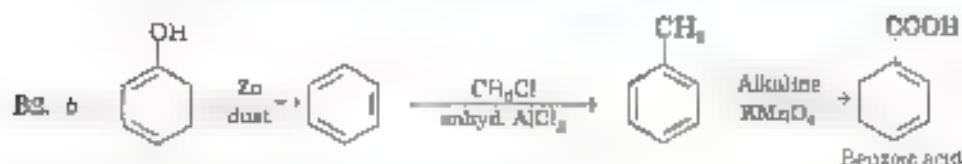


A34. (a). Alcohols react with sodium while ethers don't react



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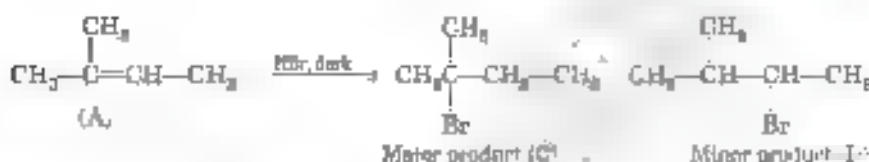
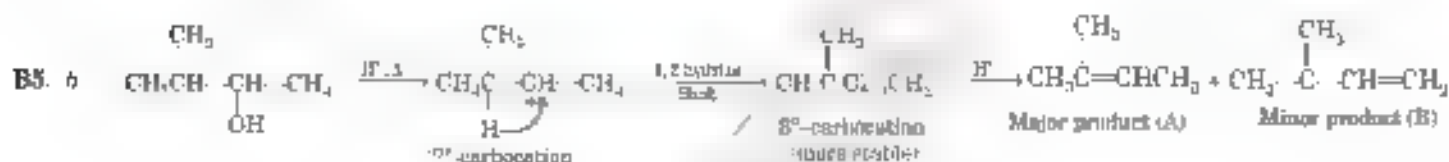
B. mcq from Competitive Examination



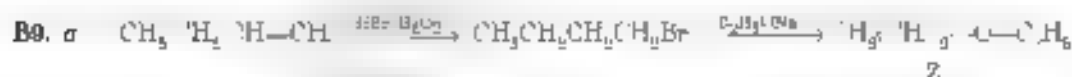
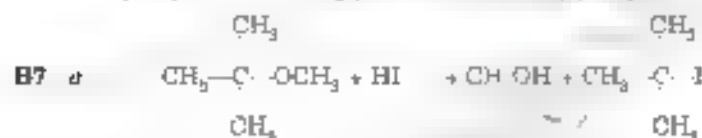
B3. d' Phenol is the most acidic among these.

B4. (c). Phenols and carboxylic acids are more acidic than aliphatic alcohols, therefore, cyclohexanol, I is least acidic. On + if two phenols, III is more acidic than IV because of the presence of three electron withdrawing NO_2 groups on the benzene ring which make C-H bond as highly polarised. Acetic acid, II is more acidic than phenols and cyclohexanol but less acidic than trinitrophenol.

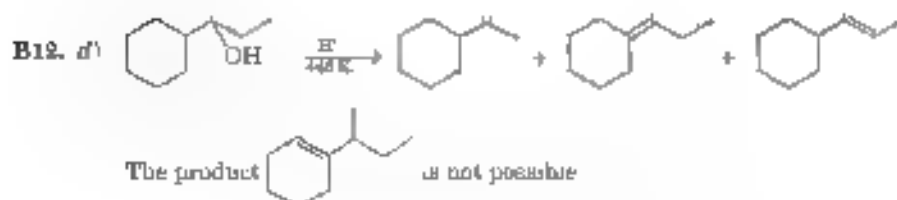
Therefore, correct order is



B6. b Electron donating effect decreases in the order $-\text{H} > -\text{CH}_3 > -\text{NHCH}_3 > -\text{OH} > -\text{CH}_2\text{OH}$. Therefore, $-\text{CH}_2\text{OH}$ group is most strongly electron donating group and hence o - o -methyl is most reactive towards electrophilic reagent.

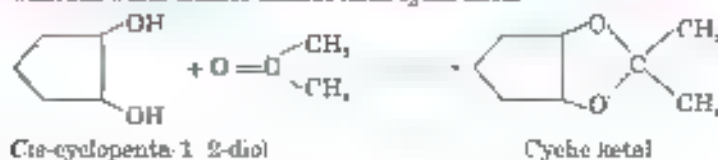


B11. (b). The reaction of phenol with chloroform in the presence of dil. NaOH is called Reimer-Tiemann reaction.

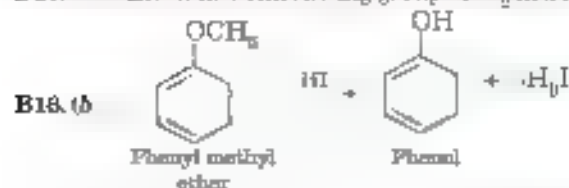


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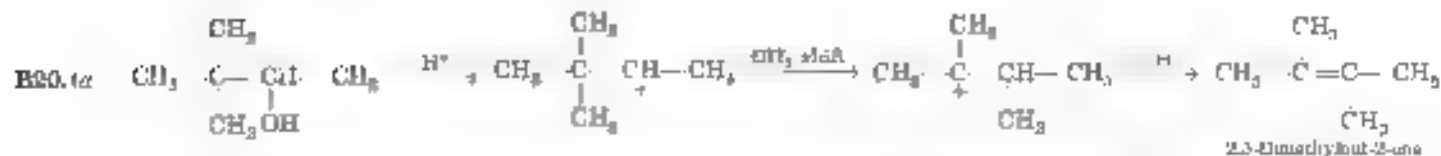
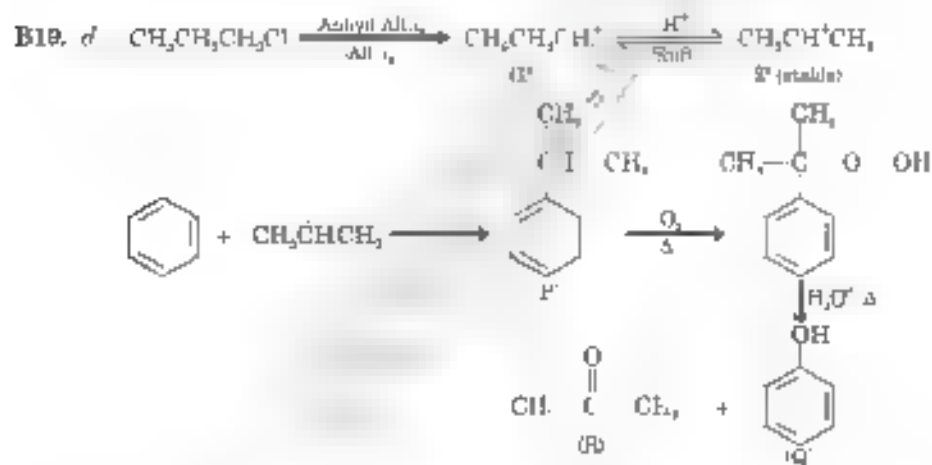
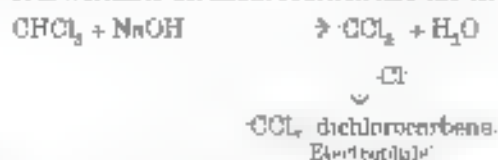
- B18. (c)** Acetone can be used to distinguish between *cis*- and *trans*-diols. *Cis*-cyclopentane-1,2-diol forms cyclic ketal with acetone, whereas *trans*-isomer cannot form cyclic ketal.



- B18. (c)** Electron withdrawing group NO_2 increases the acidity of phenol.



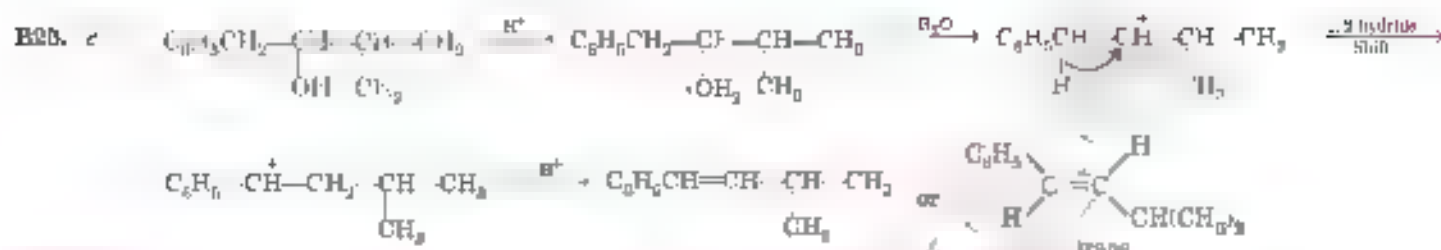
- B17. (d)** It is a Reimer-Tiemann reaction and the electrophile is dichlorocarbene CCl_2 .



- B21. (c)** Primary alcohol (pentan-1-ol) readily forms ethers when heated with conc. H₂SO₄ and gives best yield.



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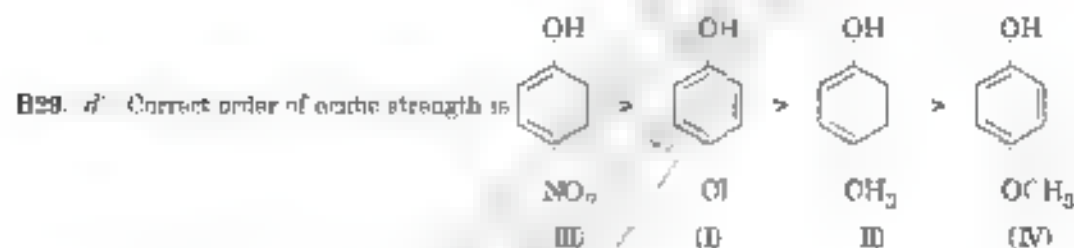
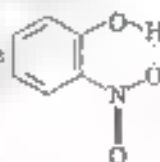
NOTE

Dehydration occurs in such a way that the double bond comes in conjugation with the C_6H_5 group.

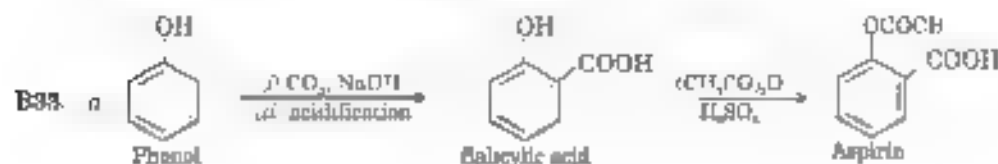
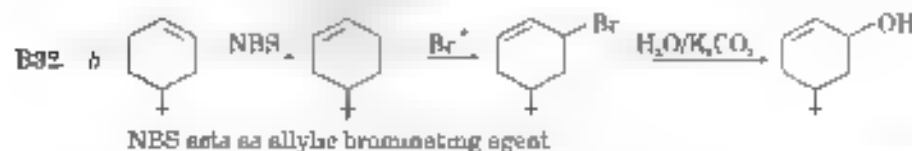
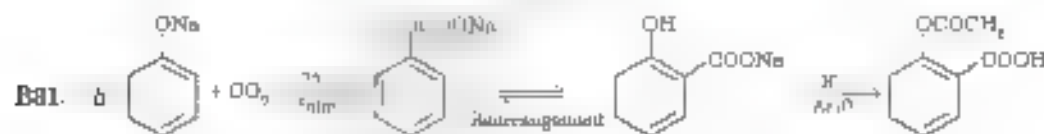
B26. (a). p -nitrophenol > m -nitrophenol > phenol > cresol

B27. d. Phenol gives violet colour with neutral FeCl_3 and benzoic acid gives buff coloured ppt

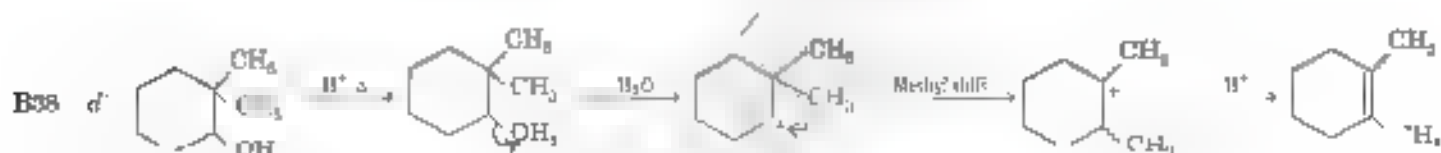
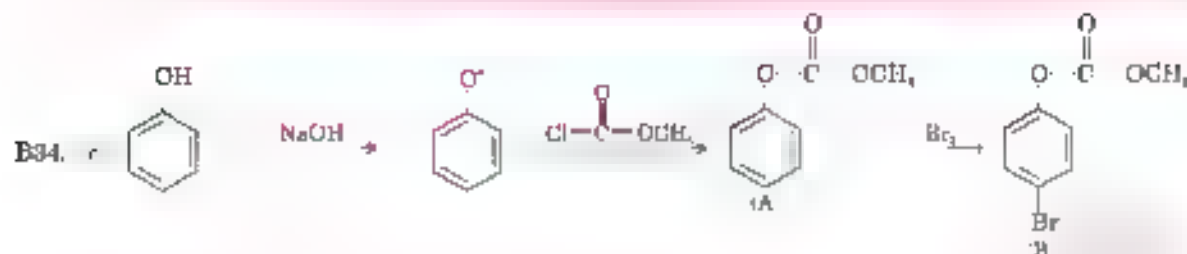
B28. a. Because o -nitrophenol shows intra-molecular hydrogen bonding as



B30. a. PCC is highly effective for oxidising 1° alcohols to aldehydes.



Competition File



B39. (c). Molecular formula can be calculated as

Element	Percentage	Atomic mass	Moles of atoms	Mole ratio
C	52	12	$\frac{52}{12} = 4.33$	$\frac{4.33}{2.19} = 2$
H	18	1	$\frac{18}{1} = 18$	$\frac{18}{2.19} = 8$
O	30	16	$\frac{30}{16} = 1.875$	$\frac{1.875}{2.19} = 1$

Empirical formula = C_2H_8O

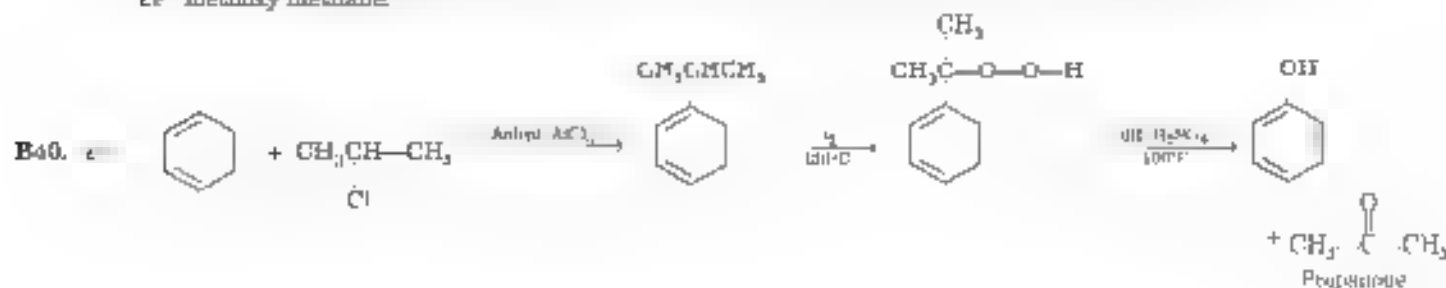
Molecular mass = $2 \times 12 + 8 \times 1 + 1 \times 16 = 46$

Empirical formula mass = $2 \times 12 + 8 \times 1 + 1 \times 16 = 46$

$$n = \frac{46}{46} = 1$$

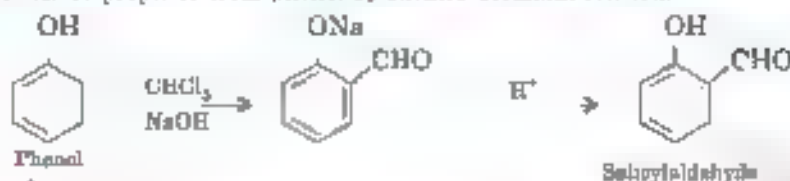
Molecular formula = C_2H_8O

Since it liberates acetylene by reacting with sodium, it is an alcohol i.e. CH_3CH_2OH . Its functional isomer is CH_3OCH_3 , i.e. methoxy methane.

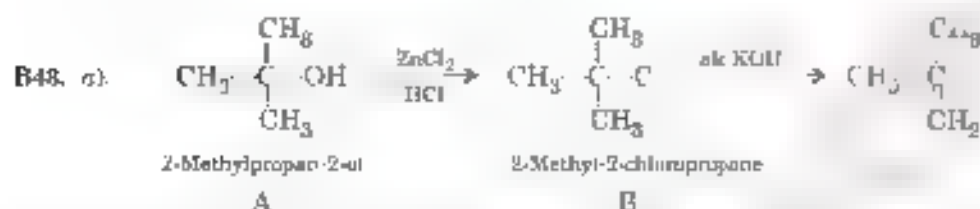
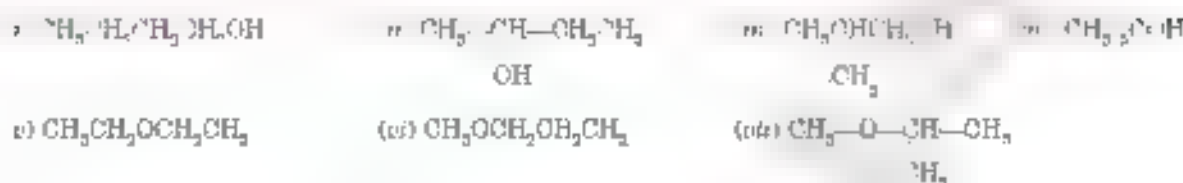


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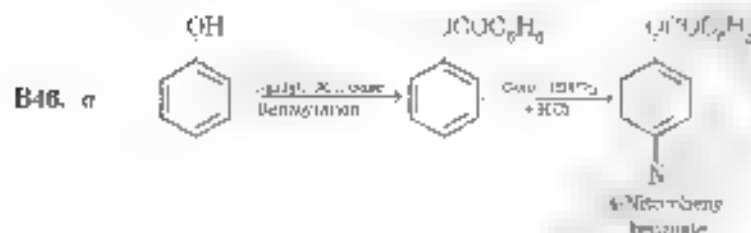
- B41. c) Salicylaldehyde can be prepared from phenol by Reimer-Tiemann reaction



- B42. b) Acyclic structural isomers are



- B43. a) Williamson's synthesis is a nucleophilic substitution reaction and proceeds via $\text{S}_\text{N}2$ mechanism.

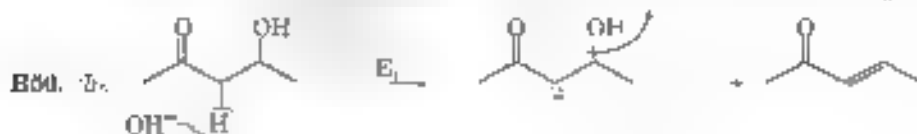


112 cm³ of CH₄ is obtained from alcohol = 0.44 g

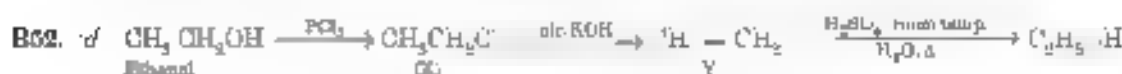
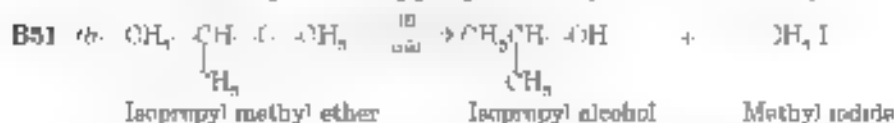
$$22,400 \text{ cm}^3 \text{ of CH}_4 \text{ will be obtained from alcohol} = \frac{0.44 \times 22400}{112} = 88 \text{ g}$$

Alcohol must be a primary alcohol because it reacts with PCl_5 to give carbonyl compound which answers silver mirror test. Therefore, (b) or (d) is correct. But (b) is correct because it has molar mass 88 g.

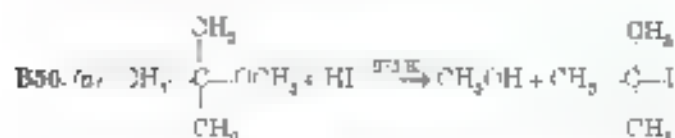
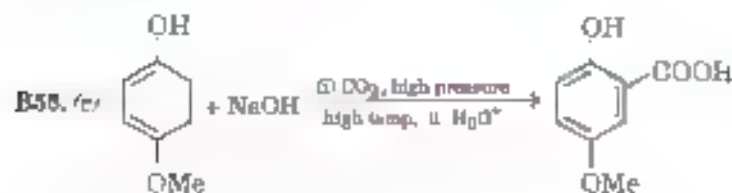
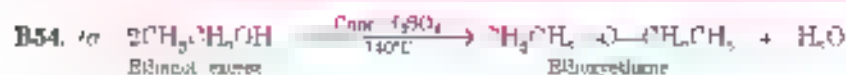
- B49. c) The order of reactivity of alcohols towards Lucas reagent is $3^\circ > 2^\circ > 1^\circ$. Therefore, 1° alcohols do not react with Lucas reagent at room temperature. The benzyl and allyl alcohols react as rapidly as 3° alcohols with Lucas reagent, because their carbocations are resonance stabilised and are stable. Thus, $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$ (1° alcohol) is least reactive.



OH⁻ is not a good leaving group but its expulsion becomes easy due to conjugated structure.

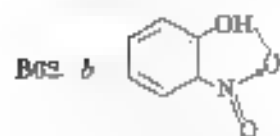
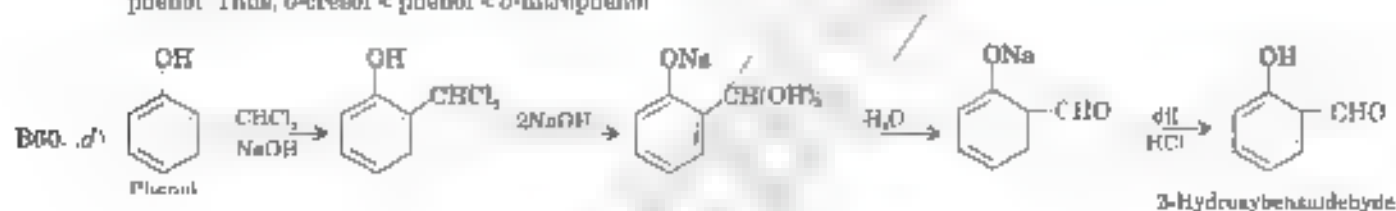


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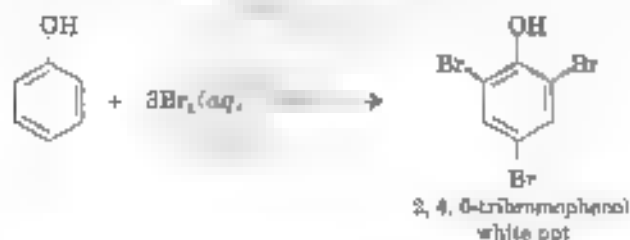


B57. (c) Acidified KMnO_4 oxidises alcohols to carboxylic acids directly. Aqueous or alkaline KMnO_4 can be used to oxidise alcohols to aldehydes.

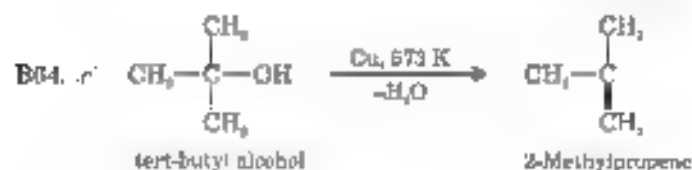
B58. (b) Electron releasing group $-\text{CH}_3$ decreases acidity of phenol and electron withdrawing group $-\text{NO}_2$ increases acidity of phenol. Thus, *o*-cresol < phenol < *o*-nitrophenol.



B63. (a) Phenol gives white precipitates with excess of bromine water due to the formation of 2, 4, 6-tribromophenol.

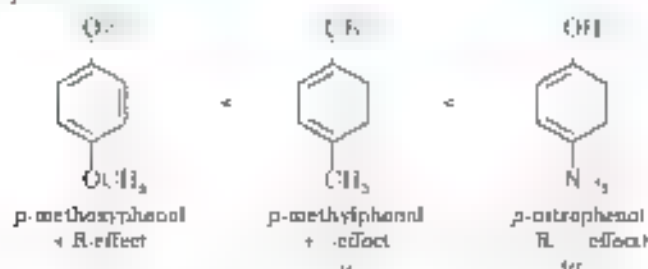


Alcohol does not react with bromine water.



Competition File

- B66. c** Electron withdrawing group increases acidic strength while electron donating group decreases the acidic strength of phenol

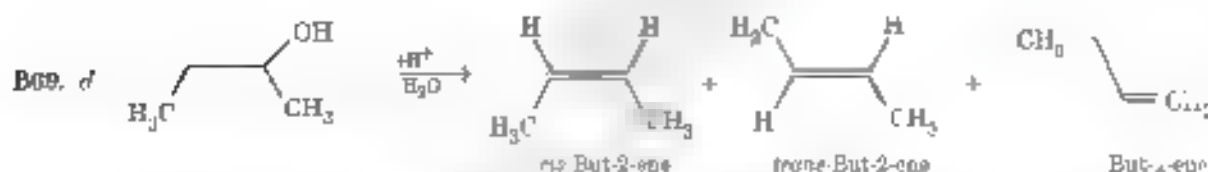
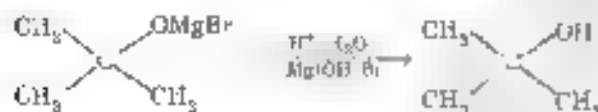
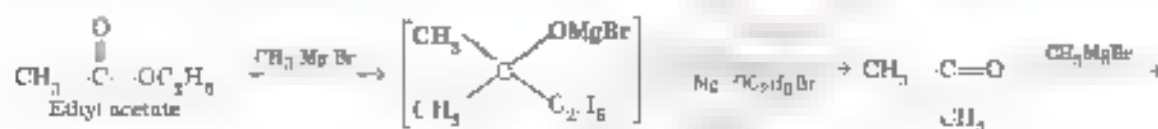


- B66. e** Long chain alcohols are successfully oxidised to aldehydes.

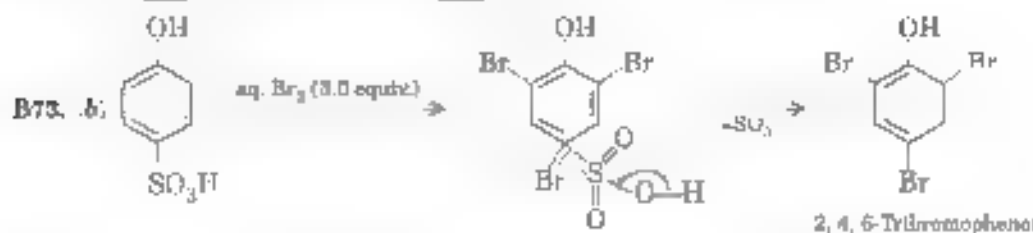
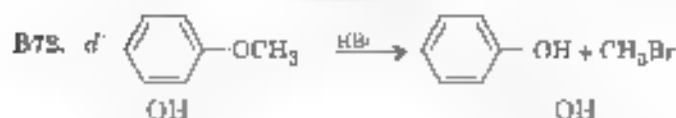
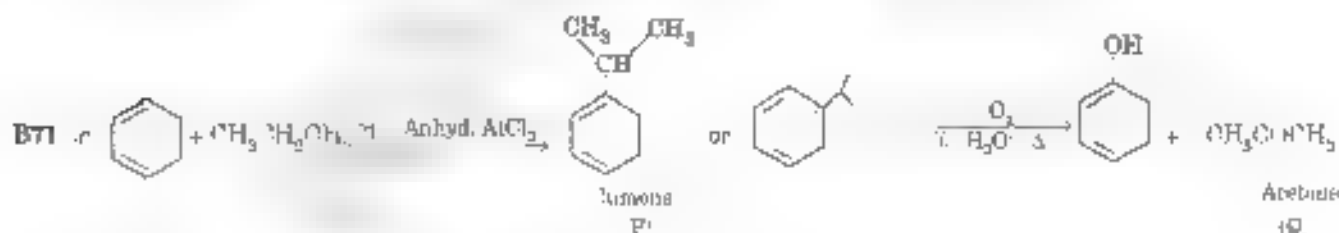


Since C-CH bond acquires partial double bond character, it will not undergo substitution.

- B68. a** Esters add two moles of Grignard reagent to form 3° alcohols. Since the Grignard reagent is CH_3MgBr , the product must contain at least two methyl groups. Therefore, the only choice having two CH_3 group is **a**




- B70. a** Increase in number of hydroxyl groups increases the boiling points. Among isomeric dihydroxy benzenes as the distance between $-\text{OH}$ & $-\text{H}$ group increases, the repulsion between them decreases and hence boiling point increases.
 I. Phenol = 181.5°C , II. catechol = 241.6°C , III. resorcinol = 281.1°C and IV. quinol = 285°C



Competition File

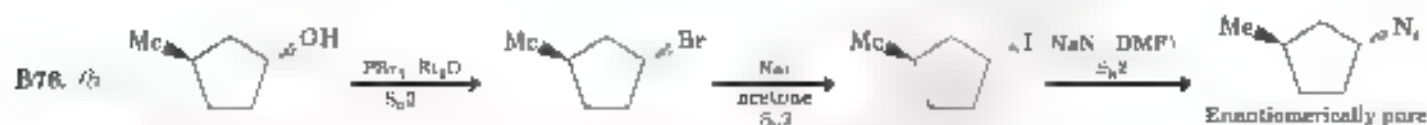
B74. c Rate of S_N1 reaction is proportional to the stability of carbocation. When two phenyl groups are replaced by two

MeO  groups, the carbocation formed will be more stable. Therefore, the reaction is the fastest.

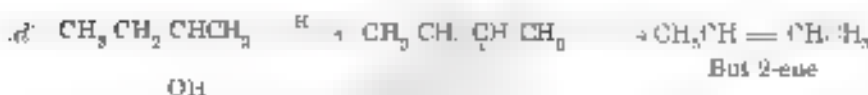
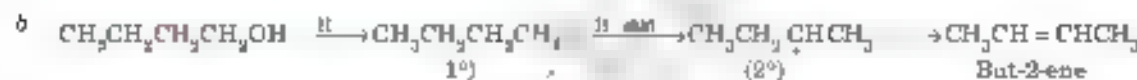
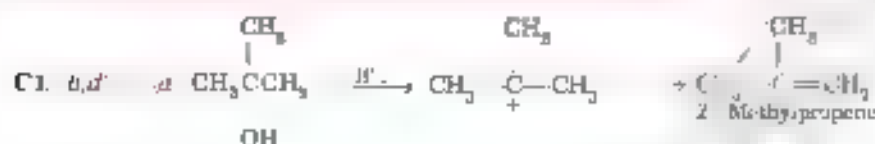


Isopropyl benzene
(Cumene)
(T)

(U)



C meq with more than one correct answer



C2. a, c Alcohols containing $\text{CH}_3\text{CH}(\text{OH})\text{CH}_3$ group, i.e. $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}(\text{OH})\text{CH}_3$ give iodoform test. Butan-1-ol

$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$ and propan-1-ol $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$ don't give this test.

C3. a, c 3,5-dinitro phenol and 4-nitro phenols are stronger acids than phenol because nitro group increases the acidity of phenols.

C4. (b, c) The reaction mechanism is

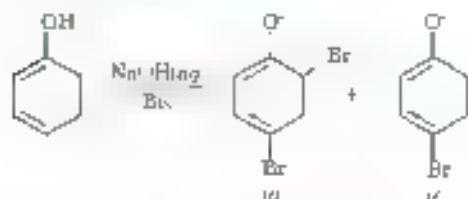


C5. b, c $^o\text{H}_2\text{C}$, ^oH and ^oOH are less acidic than phenol whereas nitrophenols are more acidic.

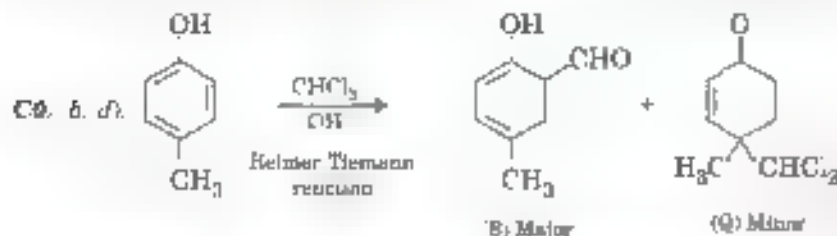


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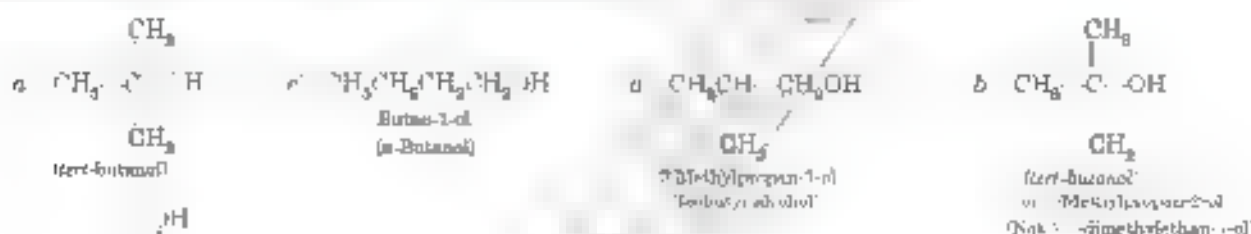
C7. a, c Phenol being acidic reacts with NaOH to form phenoxide ion. Since OH group is p -directing therefore, Br^+ enters at o - and p -positions.



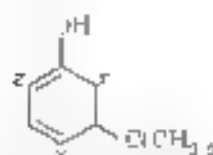
C8. b, c Boiling point decreases as branching increases. Solubility increases with branching.



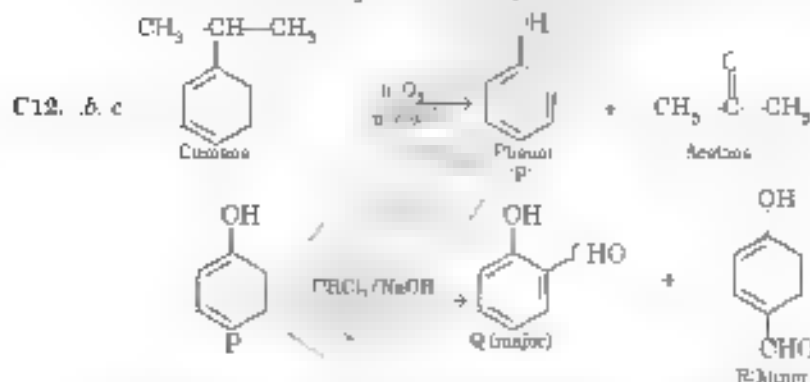
C9. a, c, d $(\text{C}_4\text{H}_{10}\text{O})$ is a monohydric alcohol $(\text{C}_4\text{H}_{10}\text{O})$. Its isomeric alcohols are



C10. a, b, c



x, y and z are suitable positions for a track as per electronic effect of CH_3 group. Due to steric effect of tert-butyl group, the bulky electrophiles are less likely to attack at positions y and z. Hence, position x is suitable for NO_2^+ , positions y and z are suitable for Br_2 . But Cl_2 being smaller can attack on the three positions i.e. x, y and z.



P forms intramolecular hydrogen bonding and R forms intermolecular hydrogen bonding. Therefore, Q has low boiling point and is steam volatile while R has high boiling point and is not steam volatile.



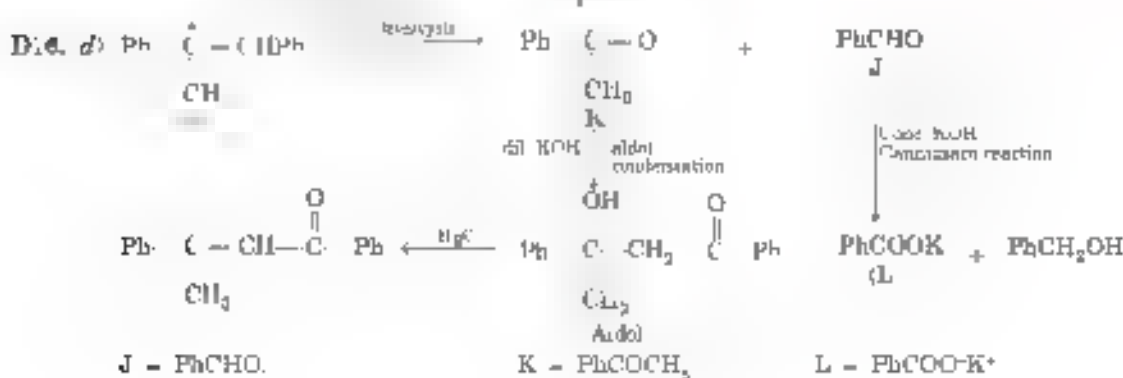
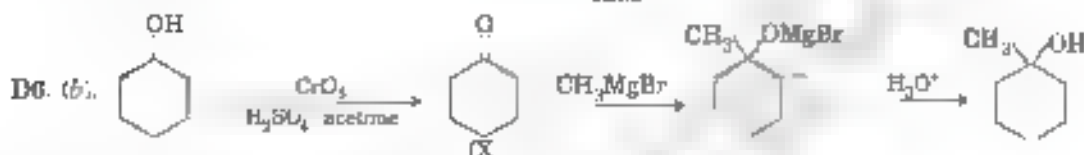
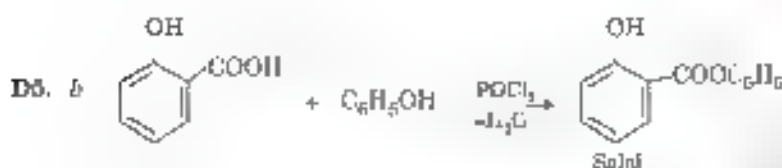
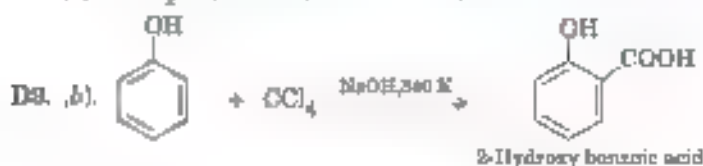
P gives dark violet colouration with 1% aqueous FeCl_3 solution because it has phenolic OH group. S gives yellow ppt with 2,4-dinitrophenyl hydrazine because it has carbonyl CHO group but does not give violet colouration with 1% aqueous FeCl_3 because it does not have OH group.

Competition File

D. mcq based on comprehension

D1. a). The reaction is Reimer Tiemann reaction.

D2. (b). SOCl_2 contains sextet of electrons and hence is a strong electrophile

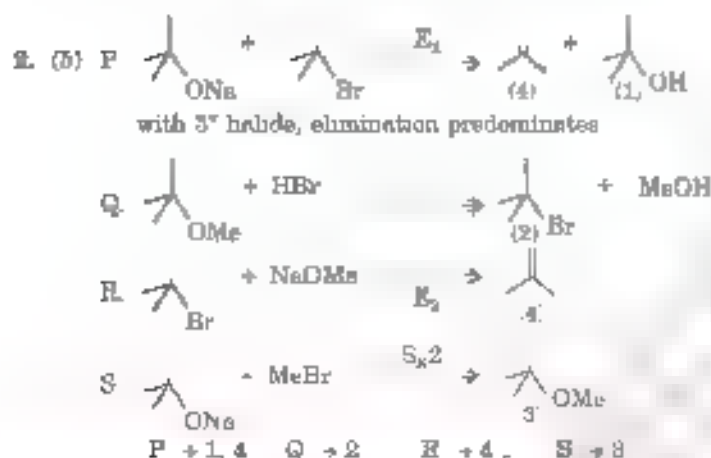
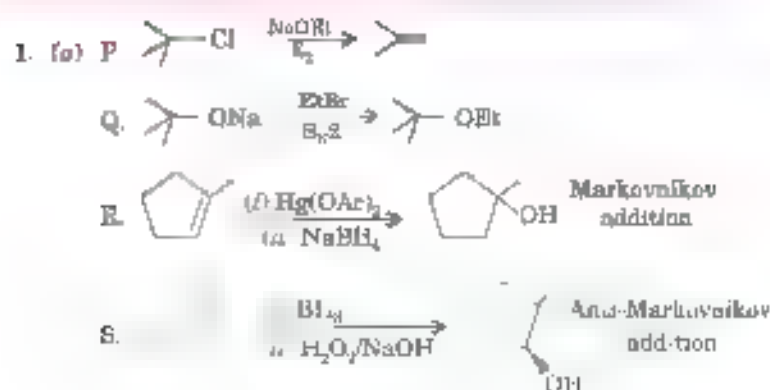


HELP

With PCC, oxidation can be stopped to aldehyde stage

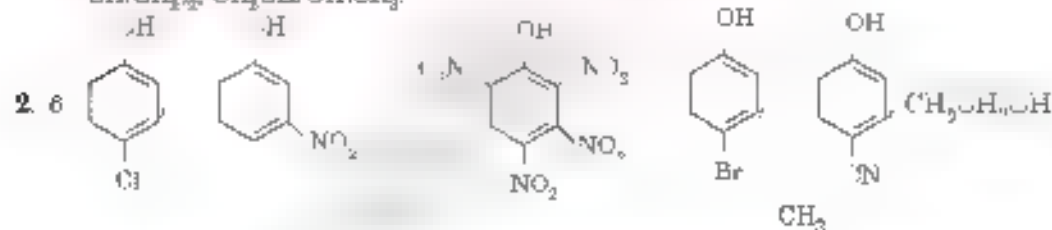
Competition File

Matching Type Questions

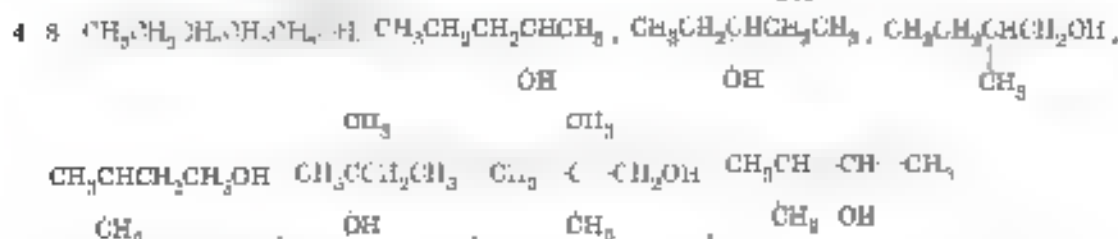


Integer Type and Numerical Value Type Questions

1. 4 Alcohols containing CH_2OH H-group give iodoform test. These are $\text{CH}_3\text{CH}_2\text{OH}$, $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}(\text{OH})\text{CH}_3$, $\text{CH}_3\text{CH}_2\text{CH}(\text{OH})\text{CH}_2\text{CH}_3$, $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$.



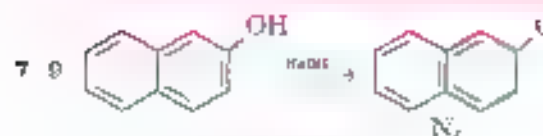
3. 1 Only tertiary alcohol gives turbidity in Lucas test. $\text{CH}_3\text{C}(\text{OH})(\text{CH}_3)\text{CH}_2\text{CH}_3$. All others will be 1 or 2.



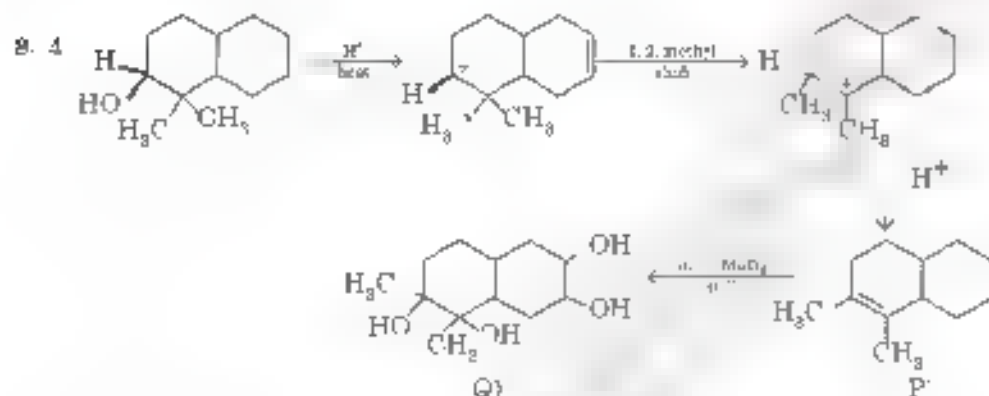
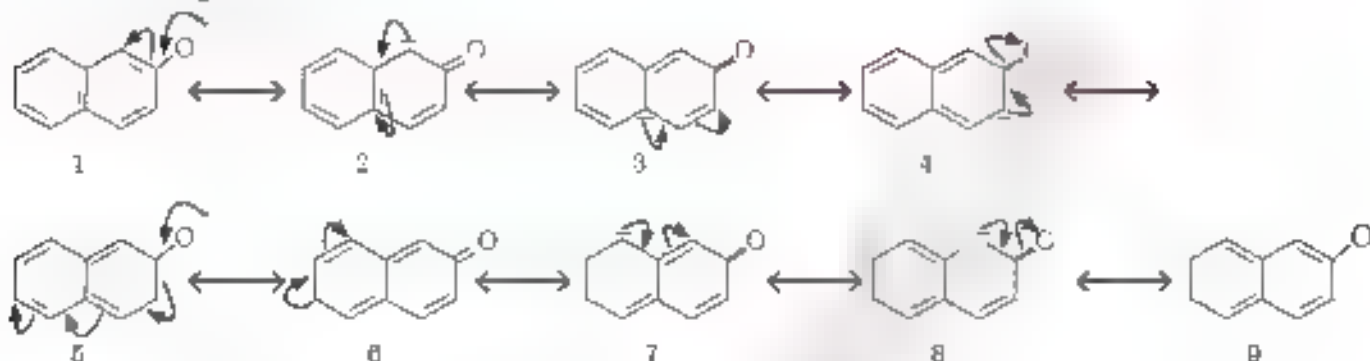
5. 2 Formaldehyde and oxirane give primary alcohols.

6. 2 Williamson's synthesis requires that the alkyl halide should be primary and alkoxide may be primary, secondary or tertiary. Hence two ethers which cannot be prepared by Williamson's synthesis are $\text{C}_6\text{H}_5\text{C}_2\text{H}_5$, $\text{C}_6\text{H}_5\text{C}_2\text{H}_5$, $\text{C}_6\text{H}_5\text{C}_2\text{H}_5$.

Competition File

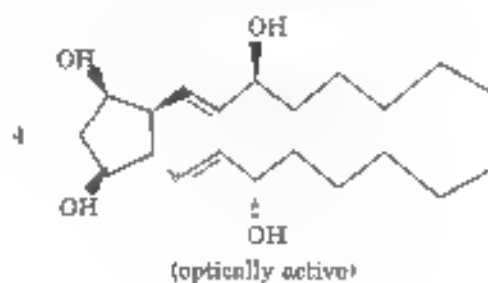
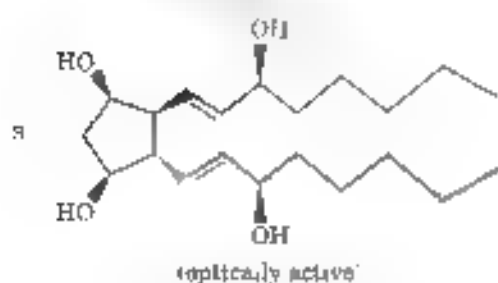
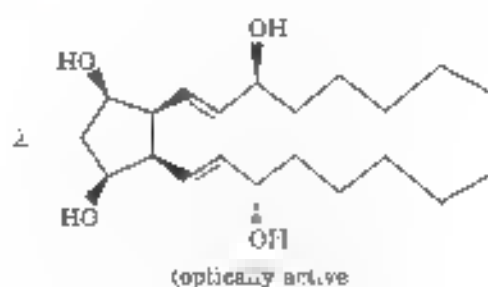
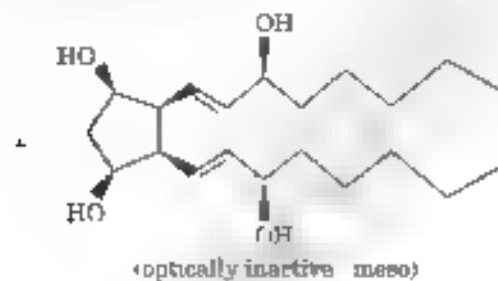


The resonating structures of N are:

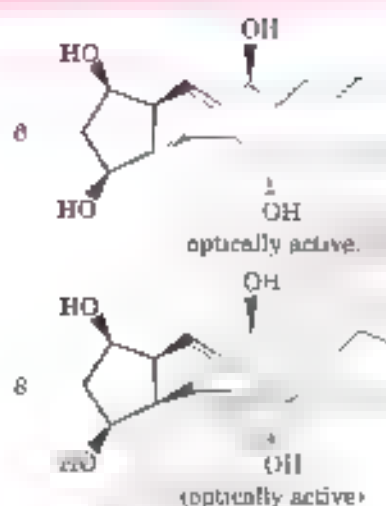
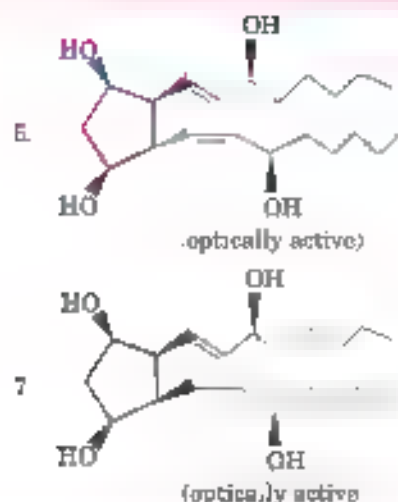


There are four hydroxyl groups in (Q).

9. 7.00 There are eight isomers and one of these is first 1 is optically inactive. Therefore, the number of optically active isomers is 7.

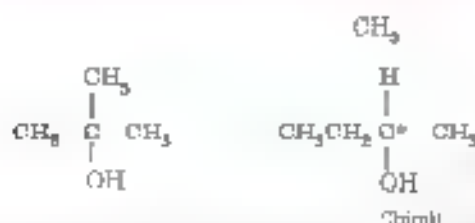


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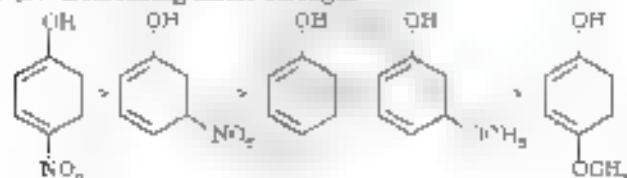


NCERT Exemplar Problems MCQs Type-I

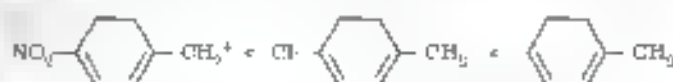
2. (a) $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$, $\text{CH}_3\text{CH}(\text{OH})\text{CH}_2\text{OH}$.



4. (c) The reagent pyridinium chlorochromate controls the oxidation to aldehyde stage.
10. (b) Weakest acid has strongest conjugate base. Since ROH is the weakest acid, therefore, RO^- is the strongest base.
11. (a) Phenol is more acidic than alcohols, therefore, it dissolves in NaOH.
12. (b) Phenol is less acidic than *o*-nitrophenol because electron withdrawing group ($-\text{NO}_2$) increases the acidic strength.
14. (b) Decreasing acidic strength



15. (c) All the three benzyl alcohols react with HBr/HCl through the formation of intermediate carbocation. More stable the carbocation, more reactive is the alcohol. The electron releasing groups i.e. NO_2 , Cl decrease the stability of the carbocation. Since NO_2 group is stronger electron withdrawing than $-\text{Cl}$ group, therefore, stability of carbocation increases in the order



Therefore, the reactivity of benzyl alcohols increases in the order $\text{II} < \text{III} < \text{I}$.

16. (a) Boiling point increases with increase in molecular mass of the alcohols. Among isomeric alcohols 1° alcohols have higher boiling points than 2° alcohols. Thus, correct order is



NCERT Exemplar Problems : MCQs Type-II

17. (a), (b), (c) Except RMgX , all other reagents reduce RCH_2OH to RCHO .
18. (a), (b), (c) Chlorobenzene does not undergo hydrolysis on treatment with NaOH at 298 K . All other three options are correct.

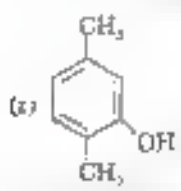
Unit Practice Test

For Detailed Instructions

Time allowed : 2 Hrs.

Maximum Marks : 85

- Write chemical equation for the preparation of phenol from chlorobenzene. 1
- Predict the products of the reaction
 $\text{CH}_3\text{CH}_2\text{CH}_2\text{OCH}_3 + \text{HBr} \rightarrow$ (1)
- Why di-tert-butyl ether cannot be prepared by Williamson's synthesis? Explain. 1
- Which of the two, phenol or o-nitrophenol are more acidic and why? 1
- What is the order of reactivity of 1°, 2° and 3° alcohols with acetic anhydride? 1
- Write the reactions and conditions involved in the conversion of
 (i) Propene to propan-1-ol (ii) Phenol to salicylic acid. (2)
- Write the IUPAC names of the following



(i)

(ii) $\text{CH}_3\text{CH}_2\text{OCH}(\text{CH}_3)\text{CH}_2\text{CH}_3$

(2)
- Write mechanism of acid dehydration of ethanol to give ethene. 1
- Which of the two, $\text{C}_2\text{H}_5\text{OH}$ or $\text{C}_2\text{H}_5\text{SH}$ is more acidic and why? 2
- Cyclo $\text{C}_6\text{H}_5\text{OH}$ has five isomers. Write their structures and names. (4)
- Write the equations involved in the following reactions
 (i) Kolbe's reaction
 (ii) Reimer-Tiemann reaction
 (iii) Williamson ether synthesis (3)
- Write chemical equations for the following reactions
 (i) Friedel-Craft's acylation of anisole
 (ii) Bromination of phenol
 (iii) Sulphonation of phenol (3)
- Give chemical tests to distinguish between
 (a) Methanol and ethanol
 (b) 1-Propanol and 2-Propanol
 (c) n-Propyl chloride and iso-propyl chloride (3)
- How will you convert the following
 (i) Propene to propan-2-ol
 (ii) Phenol to benzoic acid
 (iii) Propan-1-ol to propan-2-ol (3)
- Explain
 (i) Ethers possess dipole moment even if the alkyl radicals in the molecule are identical.
 (ii) Boiling points of ethers are lower than their corresponding alcohols.
 (iii) Ethers are relatively inert. (3)
- (a) Explain how an -OH group attached to a carbon in the benzene ring activates benzene towards 'substitution'.
 (b) Discuss the oxidation of 1°, 2° and 3° alcohols.
 (c) Explain hydroboration reaction with an example. (2,2,1)

► To check your performance, see HINTS AND SOLUTIONS TO SOME QUESTIONS at the end of Part II of the book.

ALDEHYDES, KETONES AND CARBOXYLIC ACIDS

Building on.....

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- ◆ Conceptual Questions 55, 90
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In Unit 11 we have learnt about two classes of organic compounds, alcohols and ethers, which contain functional groups containing a carbon-oxygen single bond. There are other classes of organic compounds also with functional groups containing carbon-oxygen double bond. These contain an important functional group $>C=O$ known as **carbonyl group**. The majority of biologically important compounds contain a **carbonyl group**. They are widely spread in plants and animal kingdom and play an important role in many biochemical processes of life. They are used in many food products, pharmaceutical agents and synthetic materials like perfumes, plastics, fabrics, paints, resins, adhesives, etc., needed in our everyday lives.

Name	General structural formula	Functional group
1. Aldehydes (Alkanals)	$\begin{array}{c} R \\ \\ H-C=O \end{array}$	$\begin{array}{c} O \\ \\ R \end{array}$
2. Ketones (Alkanones)	$\begin{array}{c} R \\ \\ C=O \\ \\ R \end{array}$	$\begin{array}{c} O \\ \\ R \end{array}$
3. Carboxylic acids (Alkanoic acids)	$\begin{array}{c} R \\ \\ C=O \\ \\ OH \end{array}$	$\begin{array}{c} O \\ \\ R \end{array}$
4. Acid derivatives		
(i) Acyl halides	$\begin{array}{c} O \\ \\ R-C-X \\ X = F, Cl, Br, I \end{array}$	$\begin{array}{c} O \\ \\ R \end{array}$
(ii) Acid anhydrides	$\begin{array}{c} O \\ \\ R-C-O-C-R \\ \\ O \end{array}$	$\begin{array}{c} O \\ \\ R \end{array}$
(iii) Esters	$\begin{array}{c} O \\ \\ R-C-O-R \end{array}$	$\begin{array}{c} O \\ \\ R \end{array}$
(iv) Acid amides	$\begin{array}{c} O \\ \\ R-C-NH_2 \end{array}$	$\begin{array}{c} O \\ \\ R \end{array}$

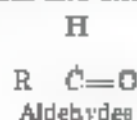
PART A

ALDEHYDES AND KETONES

Aldehydes and ketones are compounds which contain a **carbonyl group** >C=O and therefore these compounds are collectively called **carbonyl compounds**. The electronic structure of carbonyl group is

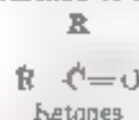


There is a double bond between carbon and oxygen. Because of difference in electronegativity between C and O, the >C=O bond is polar. In aldehydes, the carbonyl group is attached to either two hydrogen atoms or one hydrogen atom and one alkyl or aryl group whereas in ketones, it is attached to both alkyl or aryl groups. Thus,



where R may be
H, alkyl or aryl
group

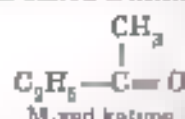
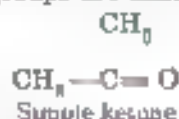
II



where R may be = R'
and alkyl or aryl
group

The functional group of aldehydes >C=O is also called **aldehydic group** while the functional group of ketones, >C=O is called **ketonic group**.

If the two groups are the same in a ketone ($\text{R} = \text{R}'$) the ketone is called a **simple ketone**. On the other hand, if the two groups are different, the ketone is called a **mixed ketone**.



NOMENCLATURE OF ALDEHYDES AND KETONES

(a) Naming aldehydes. In the **common system**, aldehydes are named according to the name of the corresponding carboxylic acid which they form on oxidation. The suffix **-ic acid** of the name of the acid is replaced by **aldehyde**. For example CH_3CHO derived from acetic acid CH_3COOH is named as **acetaldehyde**.

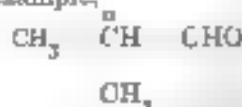


Acetic acid -ic acid + aldehyde = Acetaldehyde

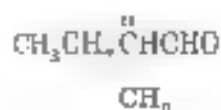
Branching in the aldehyde chain if any, is indicated by the Greek letters $\alpha, \beta, \gamma, \delta$, etc. The carbon attached to the -CHO group is α , and so on, as



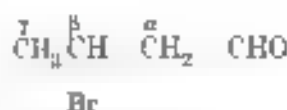
For example,



α -Methyl propionaldehyde

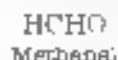


α -Methyl butyraldehyde



β -Bromobutyraldehyde

In the **IUPAC system** the aldehydes are known as **alkanals**. The name of aldehyde is derived by replacing the terminal **-e** of the name of corresponding alkane by **-al**. For example,



Alkane -e + al
= Alkanal

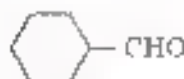
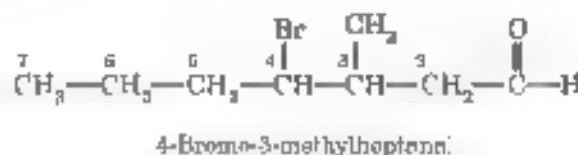
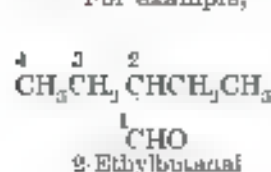
The branched chain aldehydes are named by the following **rules**

The longest chain containing the -CHO group is considered as the parent chain and the name is derived by replacing the terminal **-e** of the name of the corresponding alkane by the suffix **-al**.

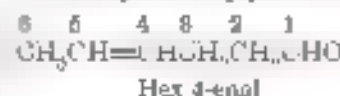
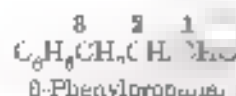
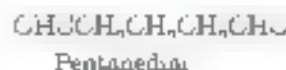
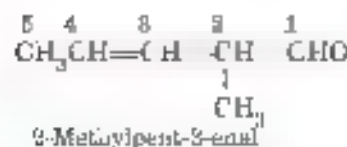
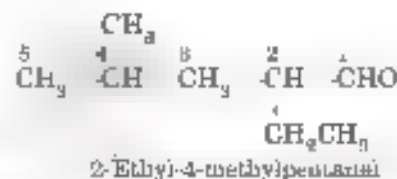
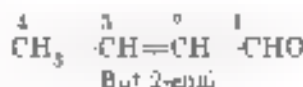
In case of substituted aldehydes, the parent chain is numbered in such a way that the aldehydic group -CHO gets lowest number i.e., 1.

The positions of the other substituents are indicated by numbers.

(iv) When the aldehyde group is attached to a ring the suffix carbaldehyde is added after the full name of the cycloalkane. The numbering of the ring carbon atoms starts from the carbon atom attached to the aldehyde group. For example,



Cyclohexanecarbaldehyde

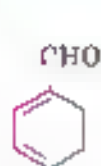


It may be noted that the carbon atom of $-\text{CHO}$ group is always assigned as number 1. Therefore, it is not necessary to indicate the position of the aldehyde group.

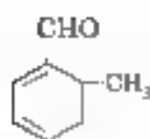
A list of common and IUPAC names of some important aldehydes are given below:

Formula	Common name	IUPAC name
$\text{H}_2\text{C=O}$	Formaldehyde	Methanal
CH_3CHO	Acetaldehyde	Ethanal
$\text{CH}_3\text{CH}_2\text{CHO}$	Propionaldehyde	Propanal
$\text{CH}_3\text{CH}_2\text{CH}_2\text{CHO}$	n-Butyraldehyde	Butanal
$\text{CH}_3\text{CHCH}_3\text{CHO}$	Isobutyraldehyde	2-Methylpropanal
$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3\text{CH}(\text{OCH}_3)\text{CH}_2\text{CHO} \end{array}$	α -Methoxy propionaldehyde	2-Methoxypropanal
$\text{CH}_3\text{CH}_2\text{CH}(\text{CH}_3)\text{CHO}$	α -Methyl butyraldehyde	2-Methylbutanal
$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3\text{CHCH}_2\text{CHO} \end{array}$	β -Methyl butyraldehyde	3-Methylbutanal
$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}(\text{Cl})\text{CH}(\text{CH}_3)\text{CHO} \end{array}$	β -Chloro- α -methyl butyraldehyde	3-Chloro-2-methylbutanal
$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CHO} \end{array}$	n-Valeraldehyde	Pentanal
$\text{CH}_3\text{CHCH}_2\text{CHO}$	Isovaleraldehyde	3-Methylbutanal
	3-Methyl cyclohexanecarbaldehyde	3-Methylcyclohexanecarbaldehyde
$\text{CH}_2=\text{CH}-\text{CHO}$	Acrolein	Prop-2-enal
$\text{CH}_3\text{CH}=\text{CH}-\text{CHO}$	Crotonaldehyde	But-2-enal
$\text{C}_6\text{H}_5-\text{CH}=\text{CHCHO}$	Cinnamaldehyde	3-Phenylprop-2-enal

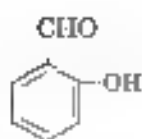
In aromatic aldehydes, $-\text{CHO}$ group is directly attached to the benzene ring. The name of the simplest aromatic aldehyde carrying aldehyde group on benzene is **benzene carbaldehyde**. However, the common name **benzaldehyde** is also accepted by IUPAC. The other aromatic aldehydes are therefore named as substituted benzaldehydes. In case of substituted aromatic aldehydes, the positions of the substituents in benzene ring with respect to $-\text{CHO}$ group are indicated either by suffixes *ortho*, *meta* or *para* or by numbers 1, 2, 3, etc. with the carbon bearing the $-\text{CHO}$ group as number 1.



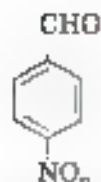
Benzaldehyde
or Benzenecarbaldehyde



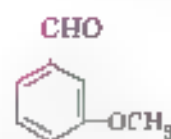
2-Methylbenzaldehyde
or Toluinaldehyde



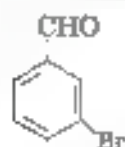
2-Hydroxybenzaldehyde
or o-Hydroxybenzaldehyde
or salicylaldehyde



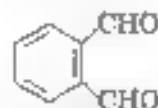
4-Nitrobenzaldehyde
or Nitrobenzaldehyde



3-Methoxybenzaldehyde
or Methoxybenzaldehyde

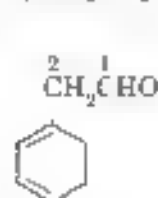


3-Bromobenzaldehyde
or m-Bromobenzaldehyde

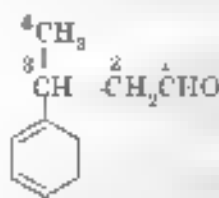


Benzene-1,2-dicarbaldehyde
Phthalaldehyde

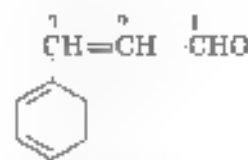
The aldehydic group may also be present in the side chain. For example,



3-Phenylpropanal
or Phenyl propionaldehyde



3-Phenylbutanal
or 3-Phenyl propionaldehyde



3-Phenylprop-2-enal
Cinnamaldehyde

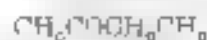
(b) Naming of ketones In the common system ketones are named by using the names of alkyl groups present in the molecule. For example,



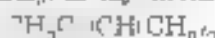
Dimethyl ketone



Methyl n-propyl ketone



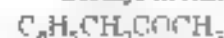
Ethyl methyl ketone



Methyl isopropyl ketone



Diethyl ketone



Benzyl methyl ketone

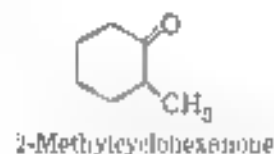
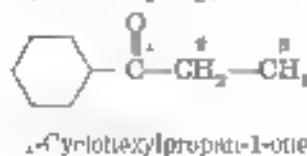
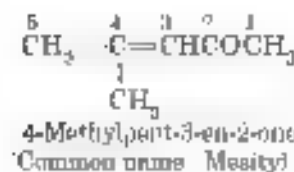
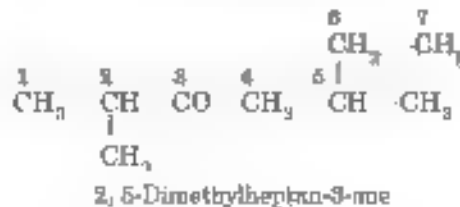
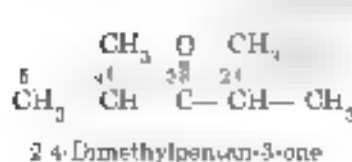
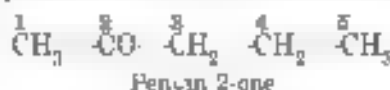
Some of the ketones are known by their old popular names as well. For example, dimethyl ketone, CH_3COCH_3 , is still popularly known as acetone.

In the **IUPAC system**, the ketones are known as **alkanones**. The individual members are named by following the general rules as

The longest chain carrying the carbonyl group is considered as the parent chain and the name is derived by replacing the terminal -e of the name of corresponding alkane by the suffix **-one**.

In case of substituted ketones, the parent chain is numbered in such a way that the **keto group gets the lowest number**.

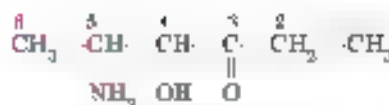
The position of the carbonyl group and the substituents is indicated by numbers. For example,



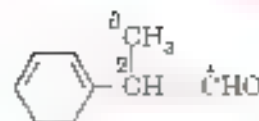


8,7-Dimethylocta-2,6-dienal

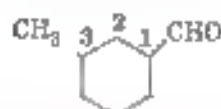
In cyclic ketones, the carbonyl carbon is given the number 1



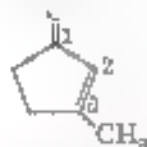
5-Amino-4-hydroxyhexan-3-one



3-Phenylpropanal



3-Methylcyclohexanone



3-Methylcyclopent-2-en-1-one



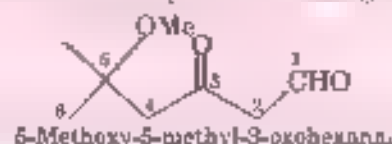
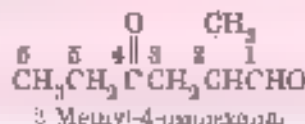
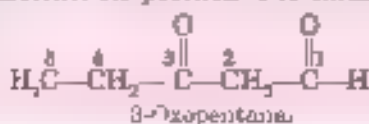
3-Methylcyclobutanone

A list of common names and IUPAC names of some important ketones are given below

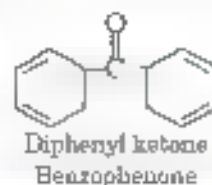
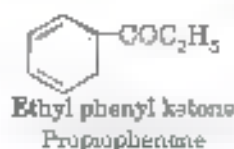
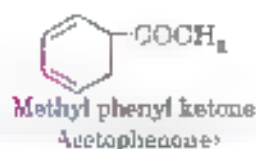
Formula	Common name	IUPAC name
CH_3COCH_3	Dimethyl ketone (or acetone)	Propanone
$\text{CH}_3\text{COCH}_2\text{CH}_3$	Ethyl methyl ketone	Butanone
$\overset{2}{\text{CH}_3}\text{COCH}_2\text{CH}_2\text{CH}_3$	Methyl n-propyl ketone	Pentan-2-one
$\overset{1}{\text{CH}_3}\text{CH}_2\overset{3}{\text{CO}}\text{CH}_2\text{CH}_3$	Diethyl ketone	Pentan-3-one
$\overset{1}{\text{CH}_3}\text{CO}\overset{2}{\text{CH}}(\text{CH}_3)\overset{4}{\text{CH}_3}$	Methyl isopropyl ketone	3-Methylbutan-2-one
$\overset{1}{\text{CH}_3}\overset{2}{\text{CH}}(\text{CH}_3)\overset{3}{\text{CO}}\overset{4}{\text{CH}}(\text{CH}_3)\overset{5}{\text{CH}_3}$	Diisopropyl ketone	2,4-Dimethylpentan-3-one
$\overset{1}{\text{CH}_3}\overset{2}{\text{C}}(\text{O})\overset{3}{\text{CH}_2}\overset{4}{\text{C}}(\text{O})\overset{5}{\text{CH}_3}$	Acetyl acetone	Pentane-2,4-dione
$\overset{1}{\text{CH}_3}\overset{2}{\text{C}}(\text{O})\overset{3}{\text{C}}(\text{O})\overset{4}{\text{CH}_3}$	Butyryl	Butane-2,3-dione
$\text{CH}_3\text{C}(\text{O})\text{CH}(\text{COCH}_3)_2$	Mesityl oxide	4-Methylpent-3-en-2-one
	α -Methyl cyclohexanone	2-Methylcyclohexanone
	β -Methyl cyclopentanone	3-Methylcyclopentanone
	Ethylphenyl ketone	1-Phenylpropan-1-one
$\text{CH}_2=\overset{3}{\text{CH}}\overset{2}{\text{C}}(\text{O})\overset{1}{\text{CH}_3}$	Methyl vinyl ketone	But-3-en-2-one
$\text{C}_6\text{H}_5\text{CH}=\overset{3}{\text{CH}}\overset{2}{\text{C}}(\text{O})\overset{1}{\text{CH}_3}$	Benzal acetone	4-Phenylbut-3-en-2-one

REMEMBER

If the compound contains both aldehyde and ketone groups, then aldehyde group is considered as *principal functional group* and ketone group is regarded as *substituent*. It is named as prefix *oxo-* along with a number to indicate its position. For example,

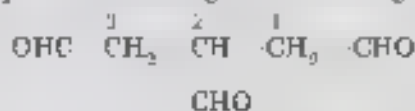


Purely aromatic or mixed aliphatic aromatic ketones are usually known by their common names. For example,

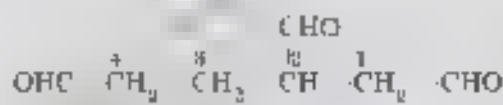


II PAC 1998 Recommendations of Aldehydes and Ketones

According to a set 1993 IUPAC recommendations, if an unsaturated chain is fitted to more than two basic functional groups, the organic compound is named as a derivative of parent alkane which does not include the carbon atoms of the functional groups. These are named by use of suffix **tricarboxylic acid** for three $-COOH$ groups, **tricarbaldehyde** for three $-CHO$ groups or **tricarbonitrile** for three $-CN$ groups. Thus, for an organic compound containing three $-CHO$ groups.

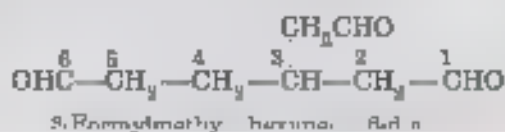


Propane-1,2,3-tricarbaldehyde
As it formerly 3-Formyl-1,5-dimethyl



Not formerly 3-Formylhexanoic, 1, 8-diol

If three groups are not correctly bonded to the α branch, a chain is made; the two side groups are considered in the parent chain, and are named by using the prefix *d.* before the *end* of the functional group. The third group forming the side chain is considered as a substituent group. For example



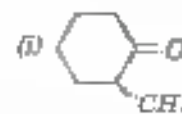
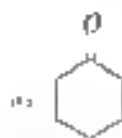
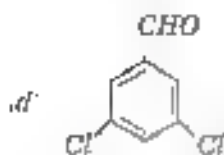
SOLVED EXAMPLES

□ **Example 1.**

Write the IUPAC names of the following compounds



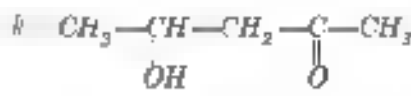
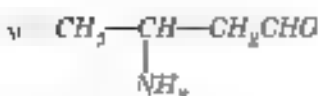
March 9, 2013



Утверждено 5.8. 2014.

Ivaga and S.B. 2018.

(He) S.H. 5018, 3018

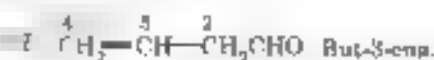
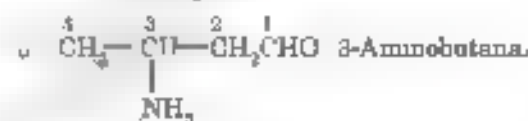
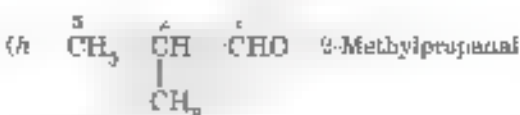
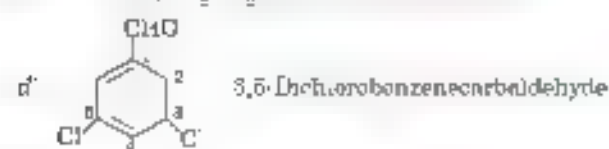
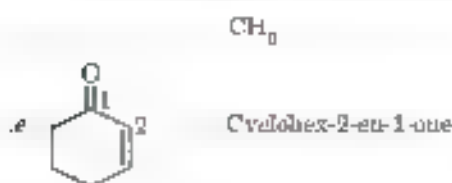


D.S.B. 2019:

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Classroom S.B. 2015

Solution : (a) $\text{CH}_3\text{CH}=\text{CHCHO}$ But-2-enal



Example 2

(a) Write the structural formulae of all the carbonyl compounds with the molecular formula $\text{C}_6\text{H}_{10}\text{O}$ and name them according to IUPAC system.

(b) Write the structural formula of the following

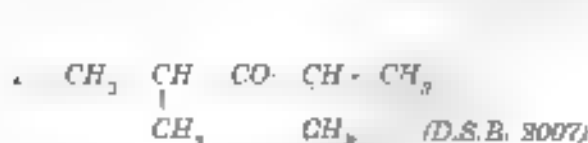
(i) 3-Phenylprop-2-enal (ii) 4-Methylpent-3-en-2-one

(iii) 3-Methylbutanal (iv) 4-Chloropentan-2-one

(CBSE Sample Paper 2007)

(A.I.S.B. 2011)

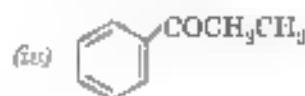
(c) Write the IUPAC names of the following compounds



(A.I.S.B. 2012)

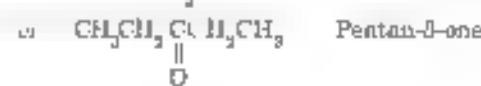
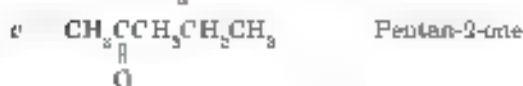


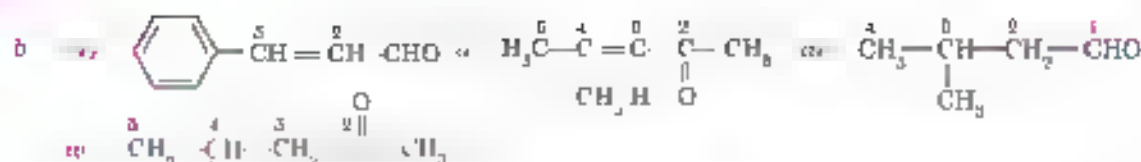
(A.I.S.B. 2012)



(Hr. S.B. 2018)

Solution : (a) The possible structures and IUPAC names are

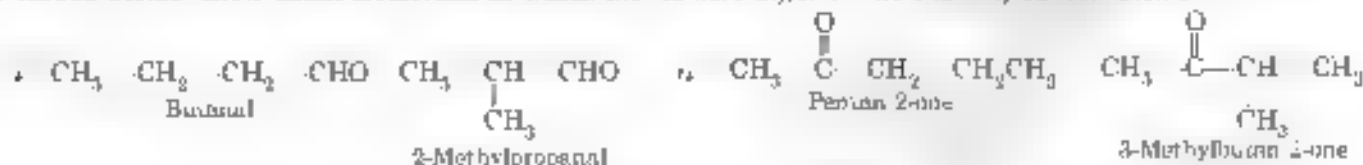




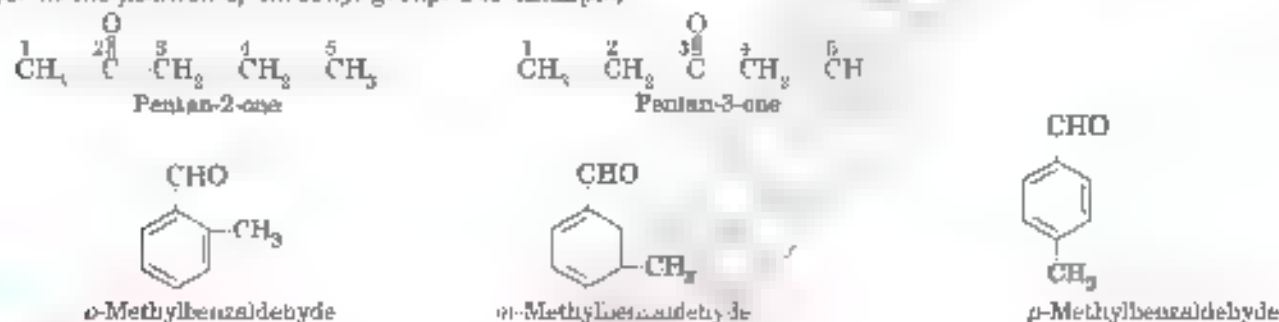
ISOMERISM IN ALDEHYDES AND KETONES

Aldehydes and ketones show the following types of isomerism :

1. Chain isomerism. Higher aldehydes containing four or more carbon atoms and ketones containing five or more carbon atoms show chain isomerism in which the isomers differ in the chain of carbon atoms.



2. Position isomerism. Higher ketones and aromatic aldehydes exhibit position isomerism in which the isomers differ in the position of carbonyl group. For example,



NOTE

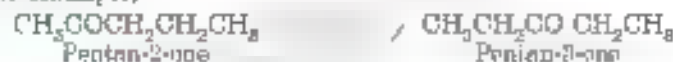
Aliphatic aldehydes do not show position isomerism because CHO group is always present at the end of carbon chain.

3. Functional isomerism. Aliphatic aldehydes and ketones are the functional isomers of each other because they have same molecular formulae but different functional groups. For example,



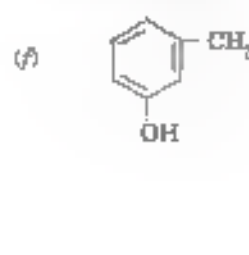
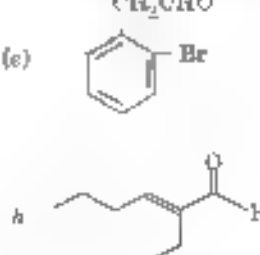
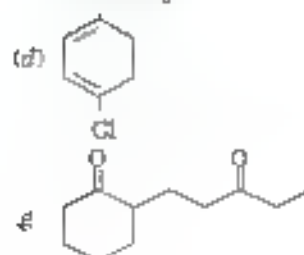
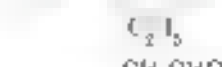
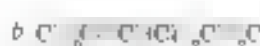
Aldehydes and ketones are functional isomers of each other

4. Metamerism. Ketones show metamerism in which the isomers differ in the alkyl groups around carbonyl group. For example,



Practice Problems

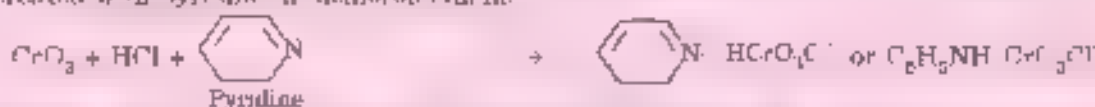
1 Give IUPAC names of the following



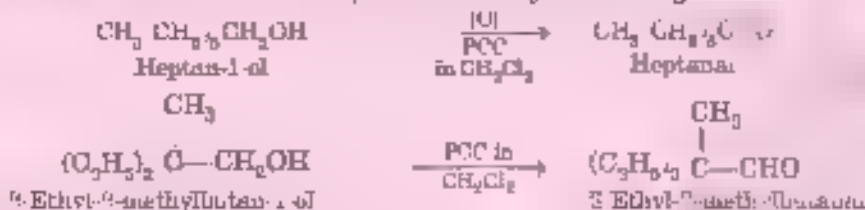
- [illegible]

Aldehydes undergo readily oxidation to carboxylic acids. Therefore, to prevent further oxidation of aldehydes, these are distilled off as soon as these are formed.

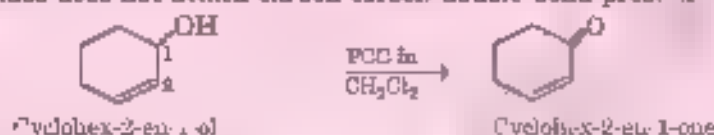
The alcohols can be converted to aldehydes stage by treating with oxidising agent: **pyridinium chlorochromate** ($C_5H_5NH^+ CrO_3Cl^-$) known as **Corey's reagent** (it is abbreviated as **PCC** and is formed when CrO_3 dissolved in hydrochloric acid is treated with pyridine or chloroacetic acid).



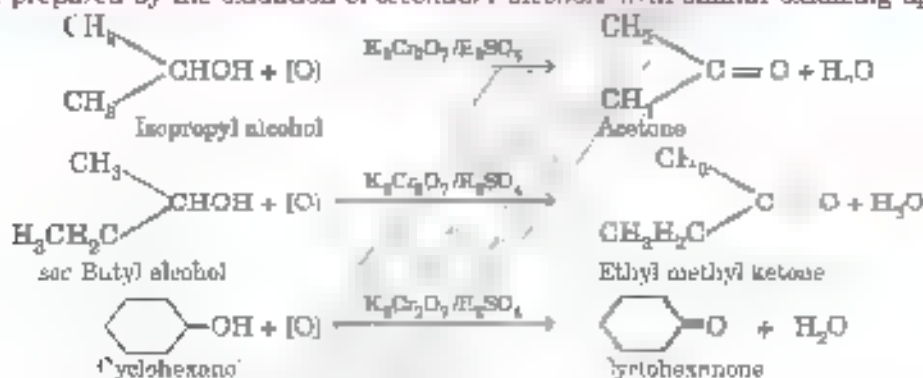
This reagent is used in non-aqueous solvent like CH_2Cl_2 or chloroform. This is a very good reagent because it checks the further oxidation of aldehydes to carboxylic acids e.g.



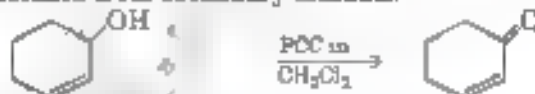
It may be noted that PCC also does not attack carbon-carbon double bond present in the molecule.



Ketones can be prepared by the oxidation of *secondary alcohols* with similar oxidising agents.

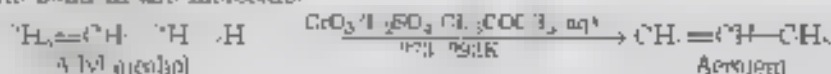


PCC can also be used to get ketones from secondary alcohols.



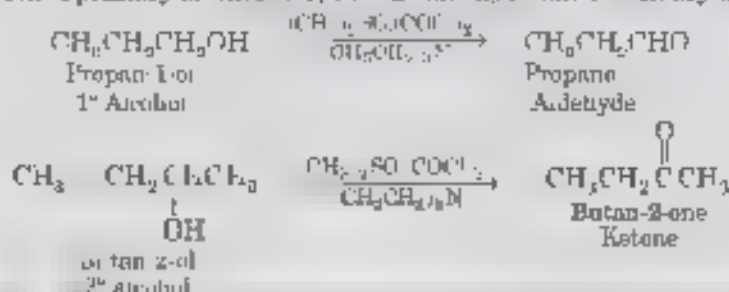
Ketones are not easily oxidised further and can therefore, be obtained in high yield by this method.

The use of CrO_3 in aqueous acetic acid is usually called **Jones oxidation** or oxidation by Jones reagent. This also does not affect double bond in the molecule.

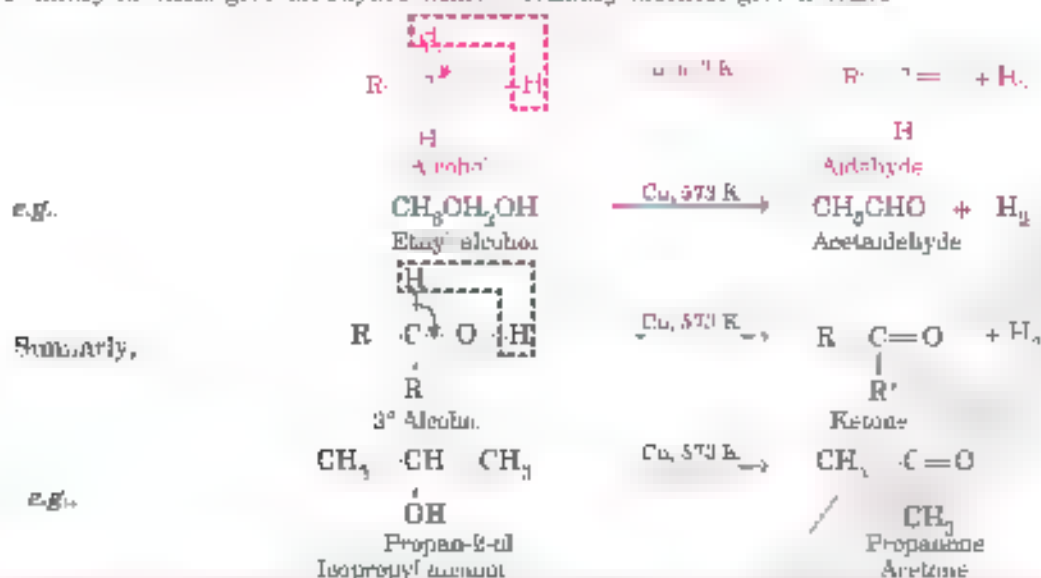


Because of the toxicity of reagents that contain chromium, a new method has been developed called

Swern-oxidation it uses dimethylsulphoxide, $CH_3)_2SO$ (DMSO), oxalyl chloride $(COCl)_2$ and triethylamine. The oxidation of primary alcohols stops at the aldehyde and secondary alcohols are oxidised to ketones.



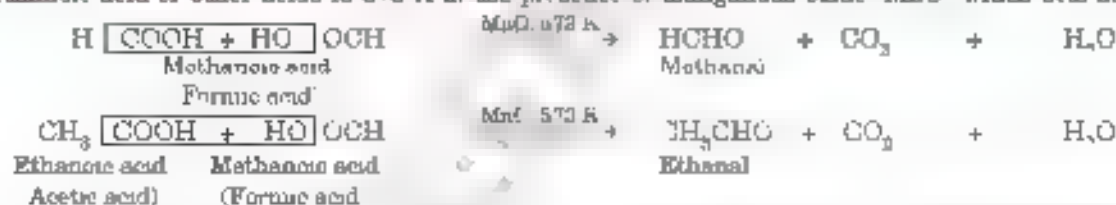
(b) **By the catalytic dehydrogenation of alcohols** Aldehydes and ketones can be prepared by the dehydrogenation of alcohols. It is carried out by passing the vapour of alcohol over reduced copper at 573 K. Primary alcohols give aldehydes while secondary alcohols give ketones.



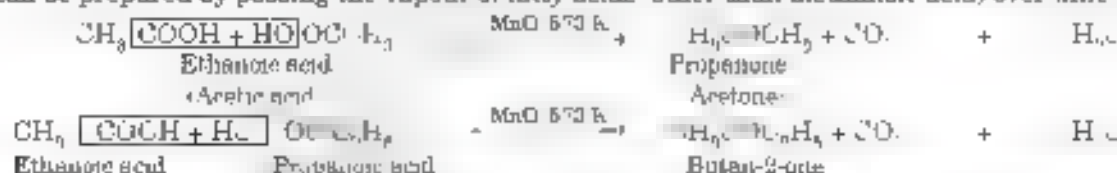
It may be noted that *tert*-alcohols cannot be dehydrogenated to get aldehydes or ketones because they do not have α -hydrogen. With Cu at 573 K, they get dehydrated to form alkenes (refer Chapter 11).

2. From Carboxylic Acids

a Aldehydes and ketones can be prepared by catalytic decomposition of carboxylic acids. This can be done by heating a mixture of methanoic acid or other acids to 573 K in the presence of manganese oxide MnO which acts as a catalyst.

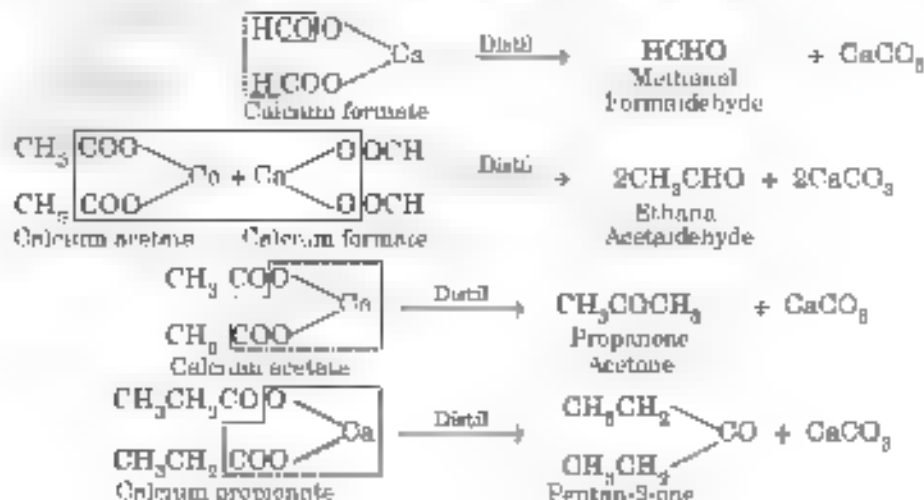


Ketones can be prepared by passing the vapour of fatty acids other than methanoic acid over MnO at 573 K.



If one of the two acids is methanoic acid, then aldehyde is always obtained otherwise ketones are formed.

b Aldehydes and ketones can also be prepared by distilling the calcium salts of the acids. For example,



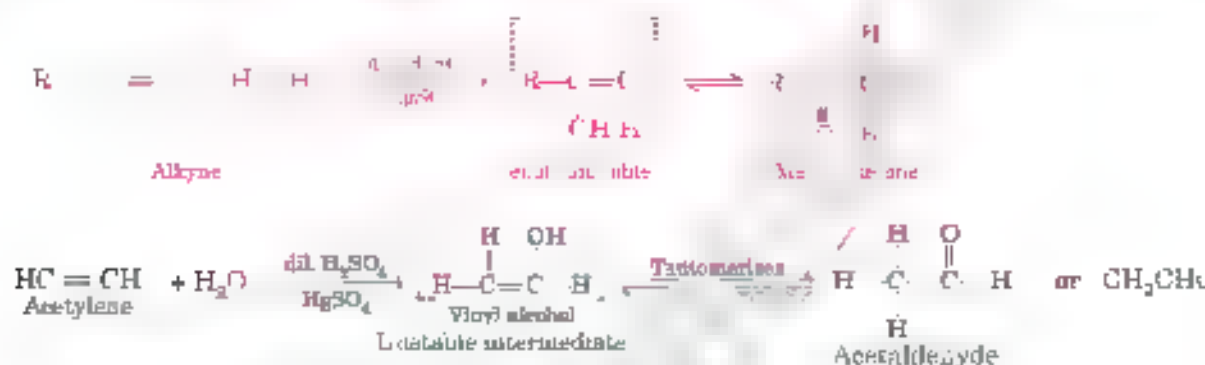
This method is, however, not very suitable for the preparation of aldehydes except formaldehyde because the yield is very low. This is because when a mixture of two calcium salts is heated three products are formed. For example, dry distillation of a mixture of calcium formate and calcium acetate gives a mixture of formaldehyde, acetaldehyde and acetone. Similarly this method cannot be used for the preparation of unsymmetrical ketone because it gives a mixture of three ketones. For example, dry distillation of a mixture of calcium acetate and calcium propionate will give a mixture of acetone, butanone and 3-pentanone.

Cyclic ketones are formed when calcium salts of dicarboxylic acids are heated. For example,

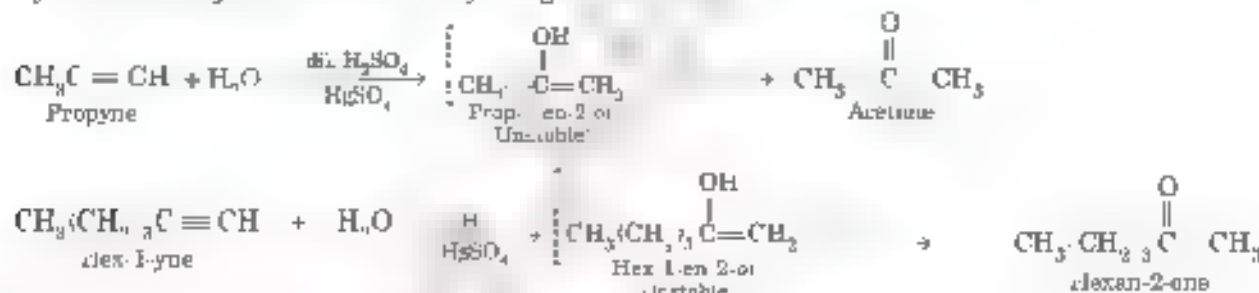


8. From hydrocarbons

(a) **By hydration of alkynes.** Aldehydes and ketones can be prepared by the hydration of alkynes in the presence of dil. H_2SO_4 and HgSO_4 as catalyst. Water adds to alkynes to form unstable enol intermediates which rearrange to form aldehydes or ketones.

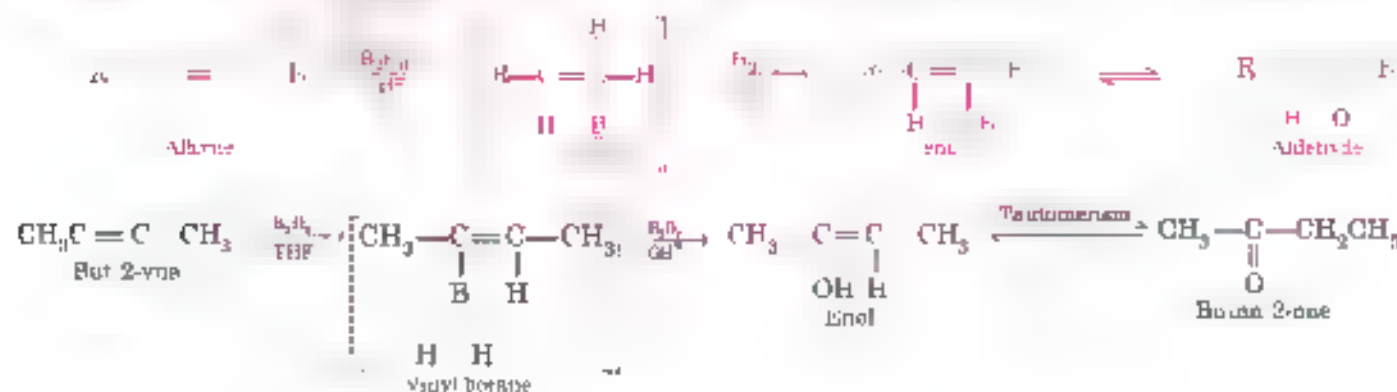


Hydration of alkynes other than acetylene gives ketones.



Formaldehyde cannot be prepared by this method

(b) **By hydroboration-oxidation reaction.** The alkynes can be converted into aldehydes and ketones by hydroboration-oxidation reaction. Borane adds to an alkyne forming vinylic borane, which on oxidation with H_2O_2 gives aldehydes and ketones. The symmetrical, non-terminal alkynes give a single ketone while unsymmetrical, non-terminal alkynes give a mixture of both possible ketones in which the methyl ketones predominate.

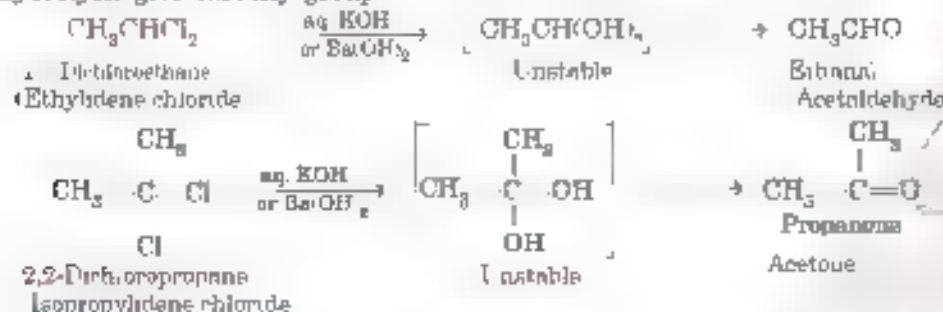


(d) By **Wacker's process**, Alkenes can be converted to aldehydes and ketones by treating with an acidified aqueous solution of palladium chloride (PdCl_2) containing a catalytic amount of cupric chloride (CuCl_2) in the presence of air or oxygen. This method is known as **Wacker's process**.



4. From Gem Dihalides

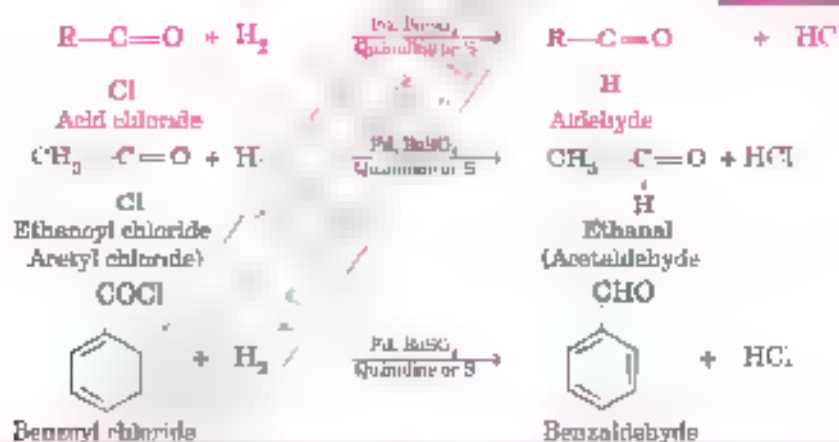
The gem dihalides, containing two halogen atoms on the same carbon atom on hydrolysis give carbonyl group.



B. Methods of Preparation of Aldehydes only

1. From Acid Chlorides

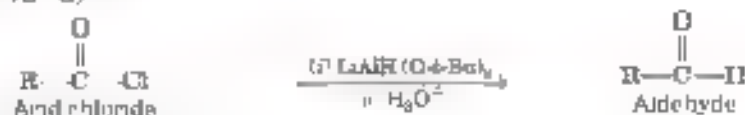
Acid chlorides are converted into aldehydes by catalytic hydrogenation in the presence of palladium (Pd) catalyst supported over barium sulphate. The catalytic mixture is **poisoned** by the addition of a small amount of sulphur or quinoline. This reaction is known as **Rosenmund reduction**.



Formaldehyde cannot be prepared by this method because its corresponding acid chloride, formyl chloride (HCOCl), is unstable at room temperature.

Function of poisoning of catalyst. Normally aldehydes are further reduced to primary alcohols. Therefore, in order to prevent the further reduction of aldehydes, the catalytic mixture is poisoned/deactivated by addition of sulphur or quinoline. This controls the reaction to aldehydes only.

Alternatively, acid chlorides can be converted into aldehydes by lithium tri-*tert*-butoxyaluminium hydride ($\text{LiAlH}(\text{O}-t\text{Bu})_3$) at 195K or 75°C ,



where $\text{LiAlH}(\text{O}-t\text{Bu})_3$ is $\text{LiAlH}_2\text{OC(CH}_3)_3$

H

2. From Reduction of Alkyl Cyanides (or nitriles) and esters

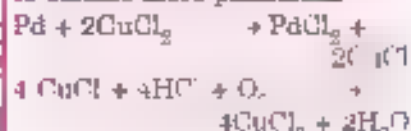
Alkyl cyanides (or nitriles) when reduced with stannous chloride and hydrochloric acid in absolute ether followed by hydrolysis gave aldehydes. This reaction is known as **Stephen reduction**.

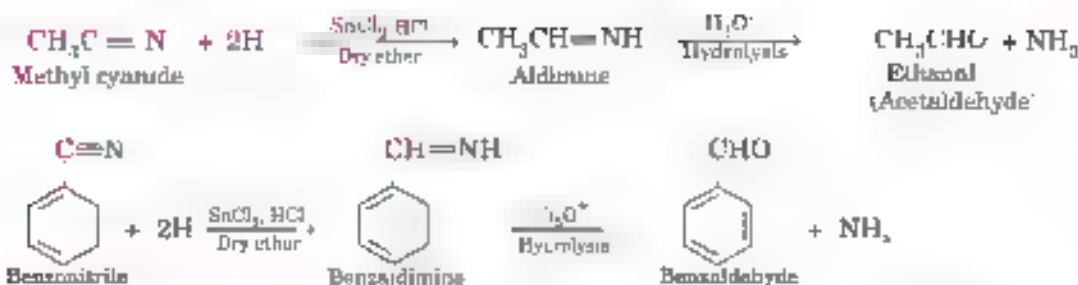
R U Curious...



Role of cupric chloride catalyst

During the reaction, Pd(II) is reduced to metallic Pd , which is ineffective for subsequent transformation. Since PdCl_2 is an expensive reagent it is better to use an external oxidising agent to convert Pd to Pd(II) oxidation state so that the reaction continues. The function of CuCl_2 is to reoxidise Pd to PdCl_2 , which is reused. During the process, CuCl_2 is reduced to Cu(I) chloride which is itself reoxidised back to CuCl_2 by oxygen so that it becomes ready to oxidise more palladium.



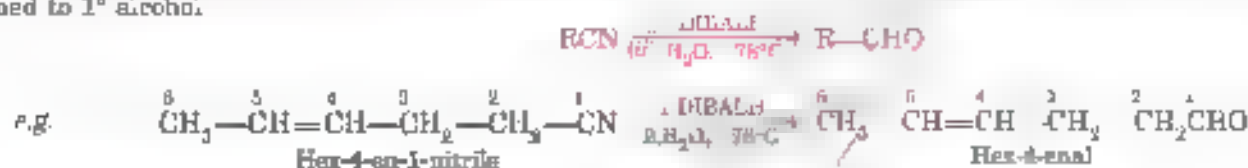


Ketones cannot be prepared by this method

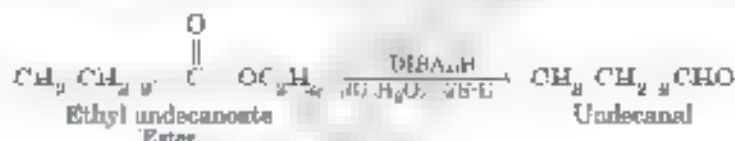
Alternatively nitriles and esters can be reduced with mild reducing agents such as diisobutylaluminium hydride (DIBALH) to imines which on hydrolysis gives aldehydes.

where DIBALH is $(\text{CH}_3)_2\text{CHCH}_2-\text{Al}-\text{CH}_2\text{CH}(\text{CH}_3)_2$

The reaction is normally carried out at a very low temperature -78° the temperature of dry ice-acetone bath. The low temperature decreases the reactivity of the reducing agent and therefore, prevents reduction of aldehyde formed to 1° alcohol.



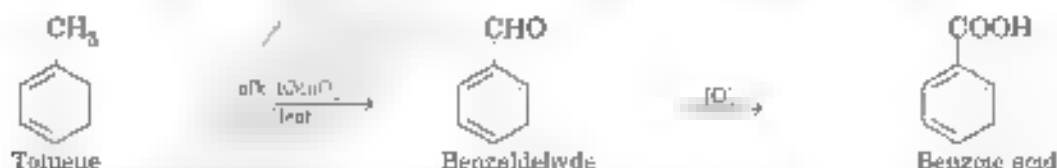
Similarly esters are reduced to aldehydes with DIBALH at low temperature -78°C



2. From aromatic hydrocarbons

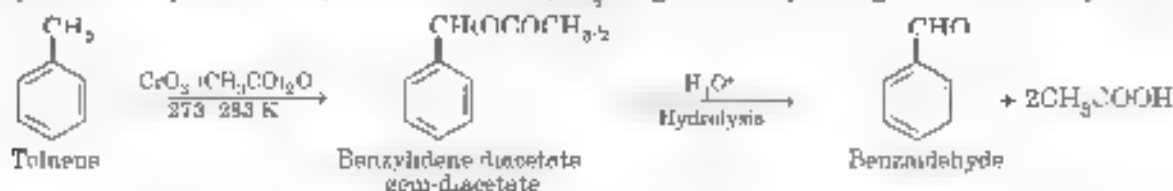
Aromatic aldehydes (benzaldehyde and its derivatives) are prepared from aromatic hydrocarbons by the following methods

(a) **By oxidation of methyl benzene** Strong oxidising agents such as acidified or alkaline KMnO_4 , acidified $\text{K}_2\text{Cr}_2\text{O}_7$, conc. HNO_3 etc. oxidise toluene and its derivatives to benzoic acid through the oxidation of intermediate aldehydes.



However, it is possible to stop the oxidation at aldehyde stage with suitable reagents which convert the methyl group to an intermediate that is difficult to oxidise further. The following methods are used for this purpose

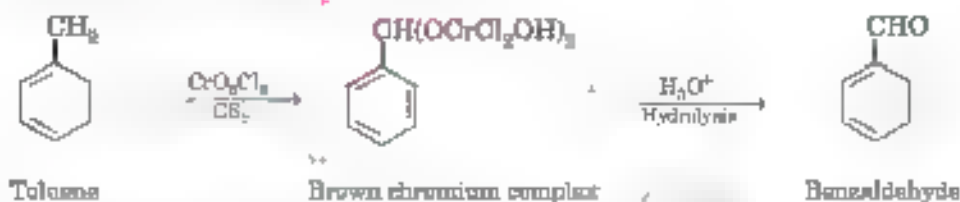
(i) **Use of chromic oxide in acetic anhydride.** Aromatic aldehydes are prepared when alkyl side chain in aromatic ring is oxidised using chromium trioxide CrO_3 and acetic anhydride. The aldehyde formed immediately gets acetylated with acetic anhydride forming gem-diacetate and this does not get further oxidised. Therefore, the fraction of acetic anhydride is to prevent further oxidation of the aldehyde to acid. The gem-diacetate formed is isolated and hydrolysed with aqueous acid (dil. HCl or dil. H_2SO_4) to give corresponding aromatic aldehyde. For example



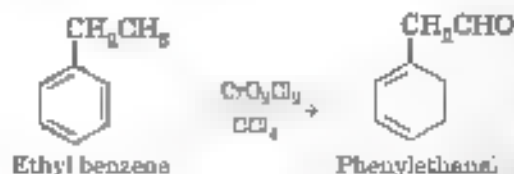
Similarly, *p*-nitrotoluene gives *p*-nitrobenzaldehyde (45% yield)

It may be noted that the further oxidation of benzaldehyde to benzoic acid is prevented by trapping the aldehyde as gem-diacetate with acetic anhydride. The gem-diacetate cannot be further oxidised.

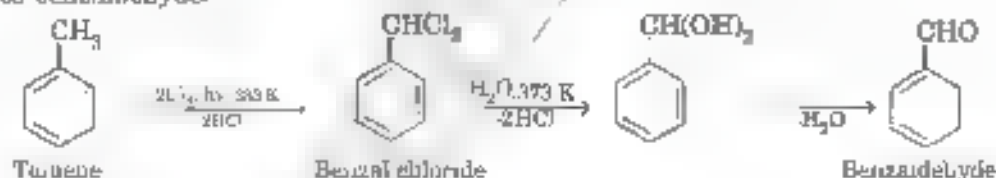
(ii) **Use of chromyl chloride.** Alkyl benzenes can also be oxidized to benzaldehyde with a solution of *chromyl chloride* CrO_2Cl_2 in CCl_4 or CS_2 . A brown chromyl complex is formed which is decomposed by water to give corresponding benzaldehyde. This reaction is called **Eaton reaction**.



In case the side chain contains group higher than $-\text{CH}_3$ group, the end carbon atom of the chain is oxidized by CrO_2Cl_2 to $-\text{CHO}$ group.

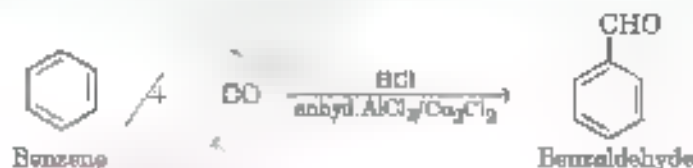


(iii) **By side chain chlorination followed by hydrolysis.** Side chain chlorination of toluene gives benzal chloride, which on hydrolysis gives benzaldehyde.



This is a commercial method used for the manufacture of benzaldehyde.

(iv) **By Gattermann Koch reaction.** Benzene or its derivatives are converted to benzaldehyde or substituted benzaldehyde by treatment with carbon monoxide and hydrogen chloride in the presence of anhydrous AlCl_3 or cuprous chloride catalyst.

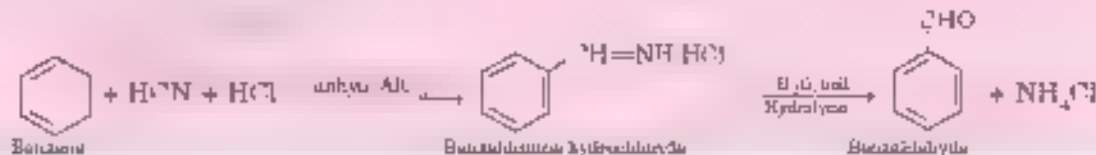


This reaction is known as **Gattermann Koch reaction**.

Gattermann aldehyde synthesis or Gattermann formylation.

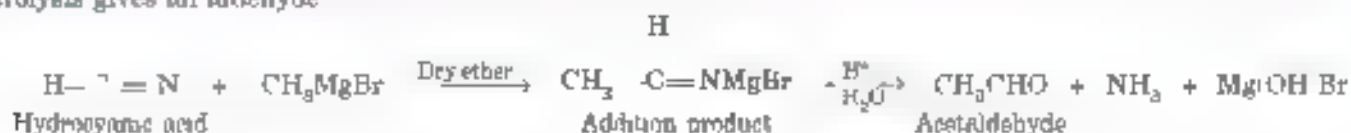
If H^+ in the Gattermann Koch aldehyde synthesis is replaced by H^+N the two are isoelectronic, the reaction is called **Gattermann aldehyde synthesis or Gattermann formylation**. This reaction proceeds through the formation of some intermediate which under the conditions of the reaction is hydrolysed to the aldehyde.

For example, when benzene is treated with a mixture of H^+N and HCl gas in the presence of anhydrous AlCl_3 , benzaldehyde is formed.



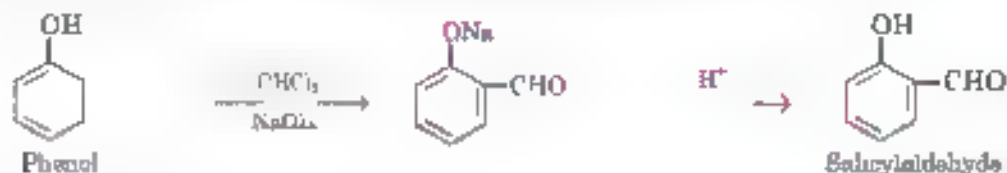
1. From hydrocyanic acid

Aldehydes can be prepared from hydrocyanic acid on treatment with Grignard reagent and subsequently followed by hydrolysis gives an aldehyde.

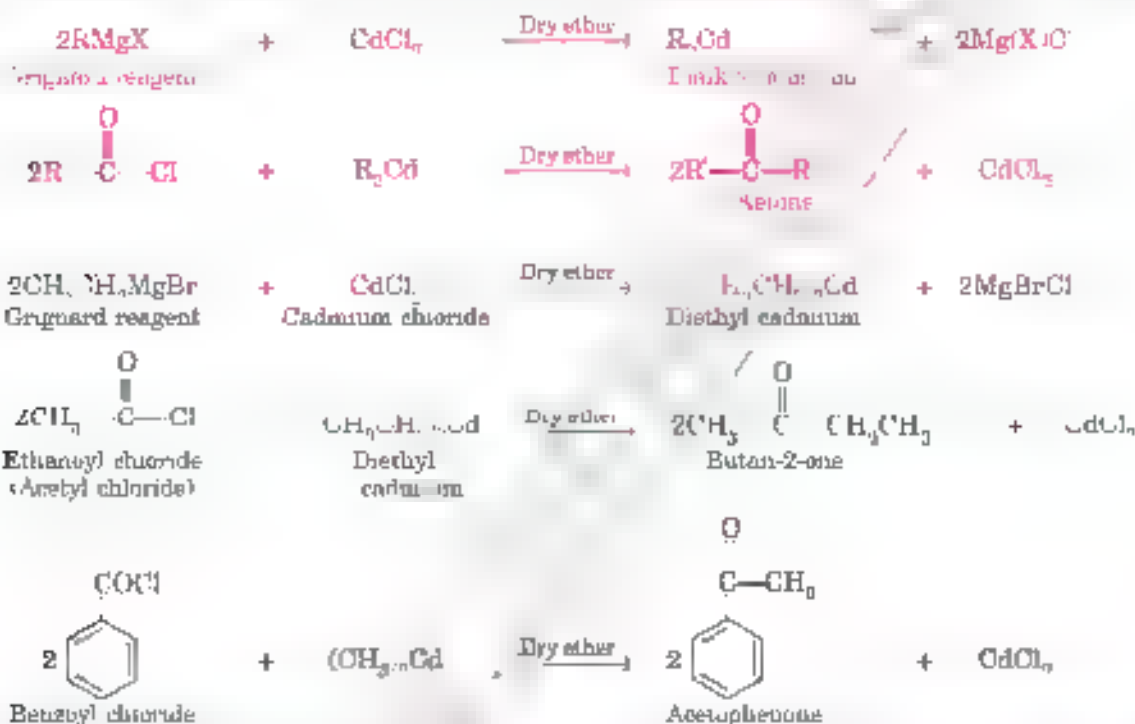


5. Reimer-Tiemann reaction

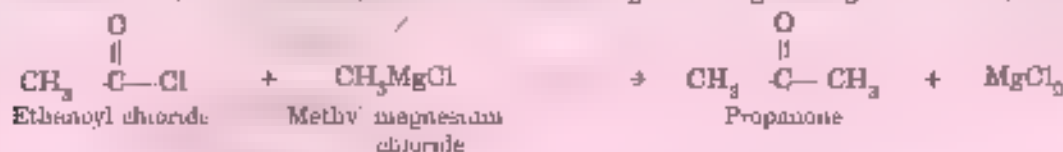
Phenolic aldehydes are obtained by treating the phenol with chloroform in aqueous sodium hydroxide solution at about 349 K. This reaction is called **Reimer-Tiemann reaction**.

**C : Methods of Preparation of ketones only****1 From acyl chlorides**

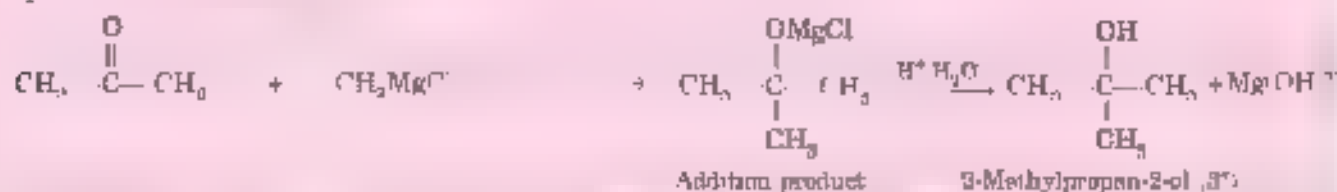
Ketones can be prepared from acyl chlorides by treating with dialkyl cadmium. The dialkyl cadmium needed for this purpose is prepared by the reaction between Grignard reagent and anhydrous cadmium chloride.



It may be noted that Grignard reagent RMgX cannot be used in place of dialkyl cadmium. This is because the ketone formed would further react with Grignard reagent to give a tertiary alcohol.



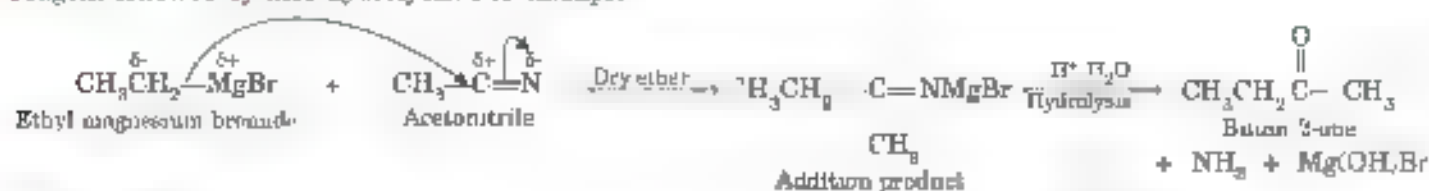
Propanone formed further reacts as



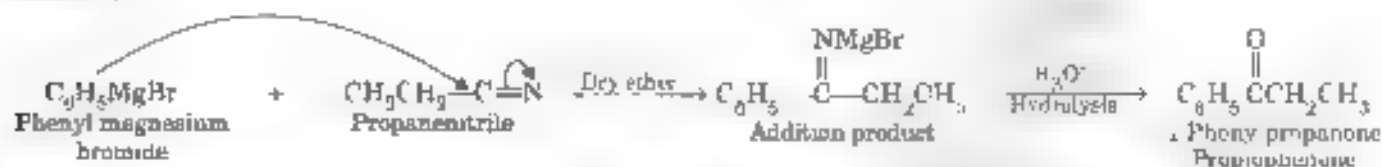
On the other hand dialkyl cadmium is weaker than Grignard reagent and has no tendency to react with ketone. Therefore, dialkyl cadmium is used for the preparation of ketones in preference to Grignard reagent.

2. From nitriles by Grignard reagent

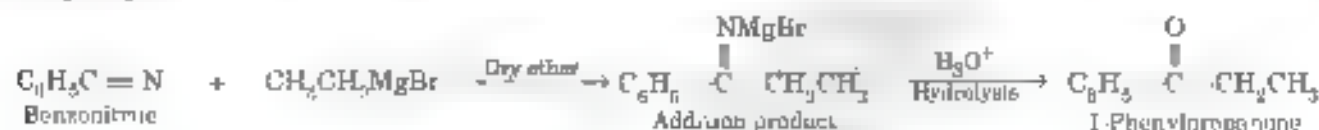
Both aliphatic and aromatic ketones can be prepared by treating an alkyl or aryl nitrile with suitable Grignard reagent followed by acid hydrolysis. For example



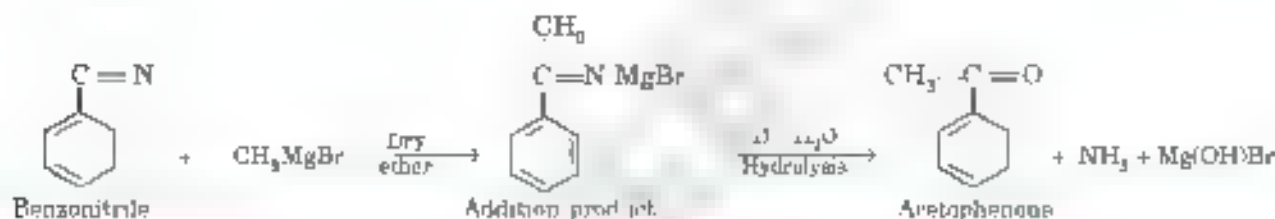
Similarly



1-Phenylpropanone can also be prepared by the action of ethyl magnesium bromide on benzonitrile followed by acid hydrolysis.



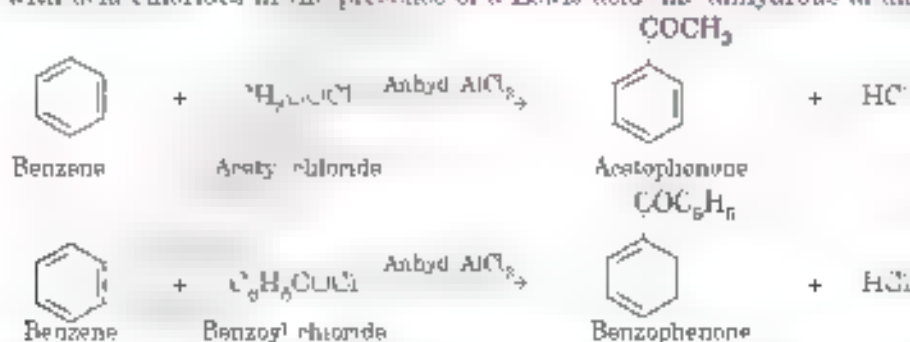
Similarly



It may be noted that if hydrocyanic acid $\text{HC}\equiv\text{N}$ is used instead of alkyl or aryl nitrile in the above reaction aldehydes are formed (already discussed).

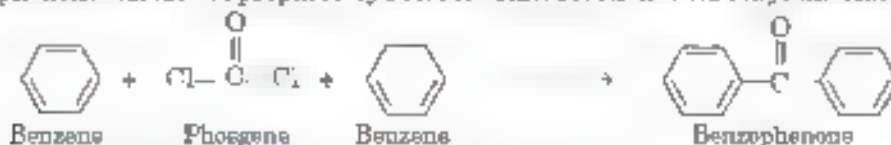
3. From benzene or substituted benzene by Friedel Crafts reaction

Aromatic ketones can be prepared by **Friedel Crafts acylation or benzoylation** by treating aromatic hydrocarbons with acid chlorides in the presence of a Lewis acid like anhydrous aluminium chloride.



Friedel Crafts reaction is a typical example of **electrophilic substitution reaction**.

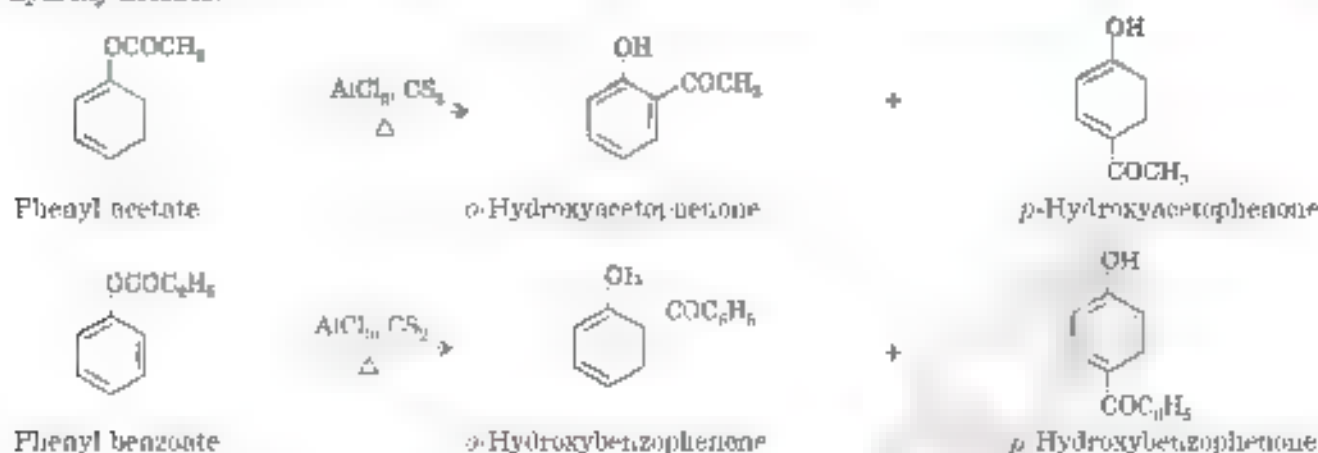
Benzophenone can also be prepared by Friedel Crafts reaction of carbonyl chloride (phosgene) with excess of benzene



4. From phenyl esters by Fries rearrangement

Phenolic esters or phenyl esters (phenyl acetate, phenyl benzoate, etc.) on heating with anhydrous AlCl_3 in the presence of CS_2 as solvent undergo a rearrangement in which the acyl, acetyl, benzoyl, etc. group migrates from

the phenolic oxygen atom to the *o*- and *p*-positions of the benzene ring to give a mixture of *o*- and *p*-phenolic ketones (or hydroxy ketones).



This reaction is called **Fries rearrangement**.

It may be noted that in this rearrangement reaction, *p*-isomer predominates at lower temperature (390 K) or less, whereas *o*-isomer predominates at high temperature (480 K) or more, due to steric effects.

PROBLEMS ON REACTIONS

Example 3

Give chemical equations for the following conversions:

(i) Cyclohexanol to cyclohexanone

But-1-ene to ethanoic

(Meghalaya S.B. 2018)

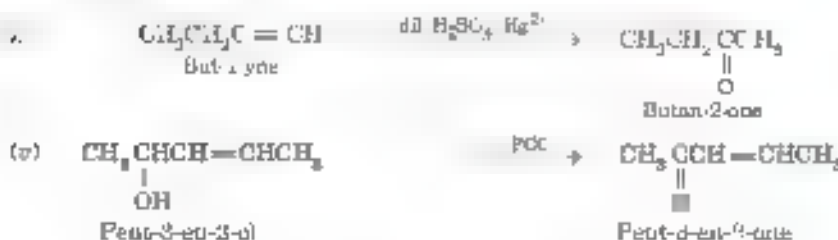
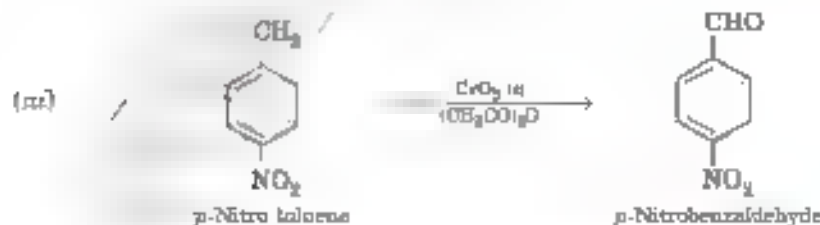
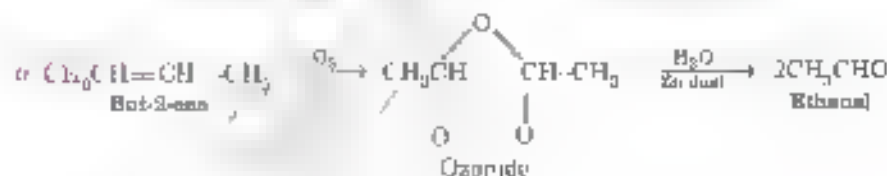
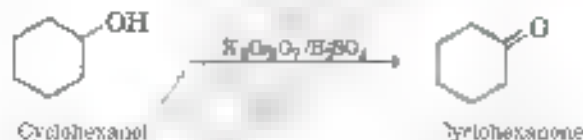
(ii) *p*-Nitrotoluene to *p*-nitrobenzaldehyde

(iii) But-1-yne to butan-2-one

(iv) Pen-3-en-2-ol to pent-3-en-2-one

(iv) Butan-1-ol to butanal

Solution : (i)



HELP

PCC does not attack carbon-carbon double bond present in the molecule.

Example 4

Suggest the reagents to bring about the following conversions

- (i) Hexan-1-ol to hexanal (ii) Cyclohexanol to cyclohexanone
 (iii) 4-Fluorobenzene to 4-fluorobenzaldehyde (iv) Ethanol to ethanal
 (v) Allyl alcohol to propenal (vi) But-2-ene to ethanal

[N.C.E.R.T.]

Solution:

- (i) $\text{C}_6\text{H}_{13}\text{NH}^+\text{CrO}_3\text{Cl}$ (PCC) in CH_2Cl_2
 (ii) $\text{K}_2\text{Cr}_2\text{O}_7$ in acidic medium
 (iii) Br_2/Fe in the presence of acetic anhydride, 275–283 K, or $\text{FeCl}_3/\text{H}_2\text{O}$
 (iv) DIBALH (Diisobutyl aluminium hydride, -78°C , H_3O^+)
 (v) PCC in CH_2Cl_2
 (vi) $\text{O}_3/\text{H}_2\text{O}$ —Zn dust

Practice Problems

8. How are the following compounds prepared?
 (a) Benzaldehyde from benzoyl chloride (b) Acetophenone from benzene
 (c) Acetone from isopropyl alcohol (d) Acetone from propyne.
9. Name the alkenes which on reductive ozonolysis gives only acetone.
- Ans. 2, 3-Dimethylbut-2-ene
10. Complete the following reactions



11. How will you obtain the following?



PHYSICAL PROPERTIES OF ALDEHYDES AND KETONES

The important physical properties of aldehydes and ketones are given below.

1. Physical state. Methanal is a pungent smelling gas. Ethanal is a volatile liquid, b.p. 204 K. Other aldehydes and ketones containing up to eleven carbon atoms are colourless liquids while still higher members are solids.

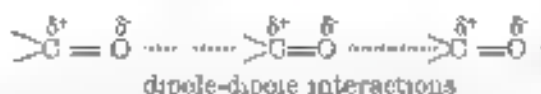
2. Smell. With the exception of lower aldehydes which have unpleasant odours, aldehydes and ketones have generally pleasant smell. As the size of the molecule increases, the odour becomes less pungent and more fragrant. In fact, many naturally occurring aldehydes and ketones have been used in blending of perfumes and flavouring agents.

3. Solubility. Aldehydes and ketones up to four carbon atoms are miscible with water. This is due to the presence of hydrogen bonding between the polar carbonyl group and water molecules as shown below.



However, the solubility of aldehydes and ketones decreases rapidly on increasing the length of alkyl chain. As a result, the higher members with more than four carbon atoms are practically insoluble in water. All aldehydes and ketones are fairly soluble in organic solvents such as benzene, ether, chloroform, alcohol, etc. The ketones are good solvents themselves.

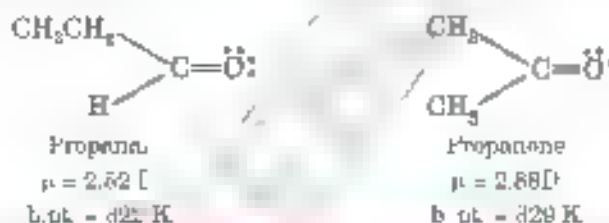
4. Boiling points. The boiling points of aldehydes and ketones are higher than those of non-polar compounds (hydrocarbons) or weakly polar compounds (such as ethers) of comparable molecular masses. However, their boiling points are lower than those of corresponding alcohols or carboxylic acids. This is because aldehydes and ketones are polar compounds having sufficient intermolecular dipole-dipole interactions between the opposite ends of $C=O$ dipoles.



However, these dipole-dipole interactions are weaker than the intermolecular hydrogen bonding in alcohols and carboxylic acids. Therefore, boiling points of aldehydes and ketones are relatively lower than the alcohols and carboxylic acids of comparable molecular masses.

Compound	$CH_3(CH_2)_3CH_2OH$ Butanol	$CH_3(CH_2)_2OCH_3$ Methoxyethane	$CH_3(CH_2)_2CH_2H$ Propan-1-ol	$CH_3(CH_2)_2H$ Propane	$CH_3CH_2COCH_3$ Propanone
Molecular mass	60	60	60	44	58
Boiling point, K	373	291	370	227	329

Among the carbonyl compounds, ketones have slightly higher boiling points than the isomeric aldehydes. This is due to the presence of two electron-releasing groups around the carbonyl carbon which makes them more polar.



Example 6

Arrange the following compounds in the increasing order of their boiling points.



[N.CERT]

Solution : The molecular masses of these compounds are comparable. $CH_3CH_2CH_2CH_2CHO = 72$, $CH_3CH_2CH_2CH_2CH_2OH = 74$, $CH_3CH_2CH_2CH_2CH_3 = 70$, $H_2N-C(=O)-H = 72$. Among these compounds, butan-1-ol ($CH_3CH_2CH_2CH_2CH_2OH$) molecules are associated because of extensive intermolecular hydrogen bonding; therefore, its boiling point would be the highest. Butanal, $CH_3CH_2CH_2CH_2CHO$ is more polar than ethoxy ethane, $C_2H_5-O-C_2H_5$. The intermolecular dipole-dipole attractions are stronger in butanal in comparison to ethoxy ethane and hence the boiling point of $CH_3CH_2CH_2CH_2CHO$ is higher than that of $CH_3CH_2CH_2CH_2CH_2OH$. n-Pentane molecules have only weak van der Waals forces of attraction which are weaker than some dipole-dipole interactions in $CH_3CH_2CH_2CH_2CHO$. Hence, boiling point of $CH_3CH_2CH_2CH_2CHO$ is slightly higher than that of n-pentane. Thus, increasing order of boiling points of these compounds is: $H_2N-C(=O)-H < CH_3CH_2CH_2CH_2CH_2CH_2CH_3 < CH_3CH_2CH_2CH_2CHO < CH_3CH_2CH_2CH_2CH_2CH_2OH$.

CHEMICAL PROPERTIES OF ALDEHYDES AND KETONES

The chemical properties of aldehydes and ketones are due to the **carbonyl group** present in their molecules.

Structure of Carbonyl Group

The carbonyl carbon is sp^2 hybridised and therefore, carbon has three sp^2 hybrid orbitals and one unhybridised p -orbital. It uses sp^2 hybrid orbitals to form three sigma bonds, one with oxygen atom of CO group, and other two with two other atoms or groups (H or R). All these three sigma bonds lie in one plane at an angle of 120° . The unhybridised $2p$ -orbital of carbonyl carbon forms π -bond with oxygen atom by overlapping sideways with half-filled $2p$ -orbital of oxygen atom. The oxygen atom has two lone pairs of electrons which occupy the remaining two orbitals. Thus, the carbonyl carbon and three atoms attached to it lie in the same plane and the π -electron cloud is above and below this plane.

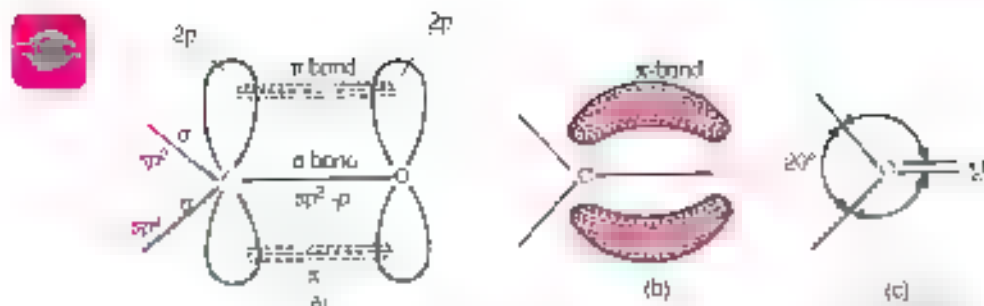


Fig. 1. Orbital picture of carbonyl group

The oxygen atom in the carbonyl group is more electronegative than carbon atom (electronegativity values $C = 2.5$, $O = 3.5$). As a result, oxygen atom tends to attract the electron cloud of the π -bond towards itself and therefore it acquires a small negative charge and carbon becomes slightly positively charged. Thus the carbonyl bond may be represented as



Hence, the carbonyl carbon is an electrophilic (Lewis acid) and the carbonyl oxygen behaves as nucleophilic (Lewis base).

The polar nature of the carbonyl group is supported by the fact that aldehydes and ketones have large dipole moments (between 2.3 D to 2.8 D). For example, the dipole moments of ethanal and propanone are 2.72 and 2.88 D respectively. The high polarity of carbonyl group is explained on the basis of resonance between the following neutral (a) and dipolar (b) structures



Differences between $C=C$ and $C=O$ bonds

The ethylenic double bond $C=C$ differs from carbonyl group $C=O$ in the following ways

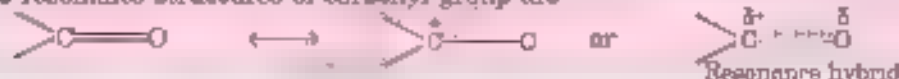
Halogens, halogen acids and H_2SO_4 undergo addition reactions with ethylenic double bond but not with carbonyl group.

- Ethylenic double bond undergoes electrophilic addition reactions while $C=O$ bond undergoes nucleophilic addition reactions.

Reasons. The main reasons for the differences in the two types of bonds are

- Carbonyl group is polar in nature while ethylenic double bond is non-polar.
- The carbonyl group shows resonance while there is no resonance in case of ethylenic double bond.

The resonance structures of carbonyl group are



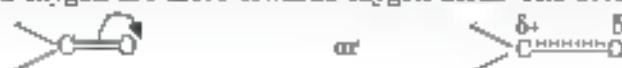
Reactions of Aldehydes and Ketones

Aldehydes and ketones are highly reactive compounds. Since both aldehydes and ketones have the carbonyl functional group, they undergo similar chemical reactions. The reactions of aldehydes and ketones can be discussed in the following categories

- Nucleophilic addition reactions
- Nucleophilic addition reactions followed by elimination of water molecule
- Oxidation reactions
- Reduction reactions
- Miscellaneous reactions

A. Nucleophilic Addition Reactions

The aldehydes and ketones undergo **nucleophilic addition reactions**. The carbonyl group is highly reactive polar group. It is polarised due to the higher electronegativity of oxygen in comparison to carbon. As a result, the electrons between carbon and oxygen are more towards oxygen atom. The actual structure may be represented as



Consequently the carbonyl carbon is positively charged while the oxygen is negatively charged. Therefore, a nucleophile Z^- attacks the electrophilic carbon atom (positively charged) of the polar carbonyl group from a direction approximately perpendicular to the plane of the sp^2 hybridised orbitals of the carbonyl group (Fig. 2). During this process, the π -electron pair between C and O gets transferred to the oxygen atom. This gives rise to an intermediate having a negatively charged oxygen. The hybridisation of the carbonyl carbon changes from sp^2 to sp^3 and a tetrahedral alkoxide intermediate is formed. This intermediate then picks up a H^+ from the medium or other part of the reagent to give the electrically neutral addition product. The net result is the addition of nucleophile and H^+ across the carbon-oxygen double bond.

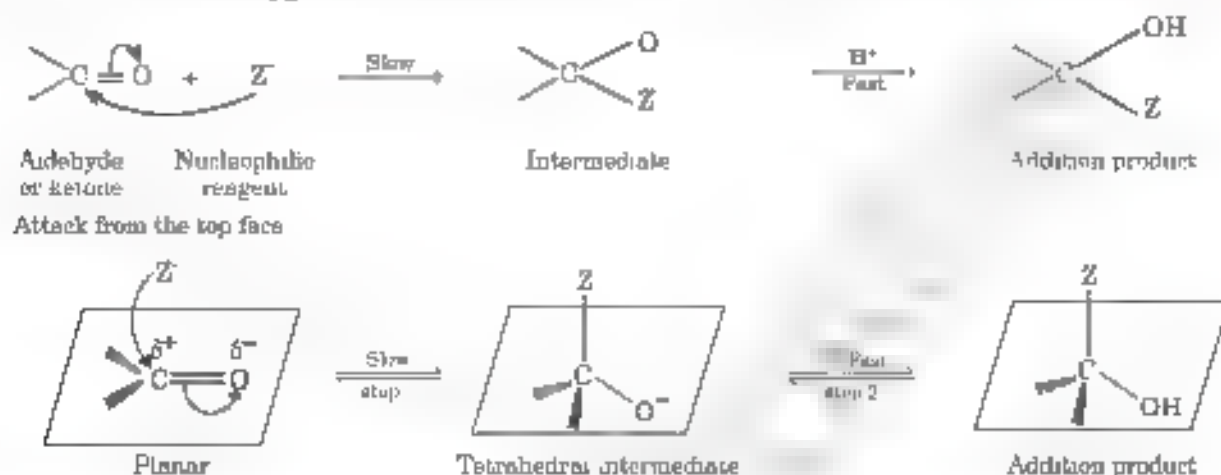
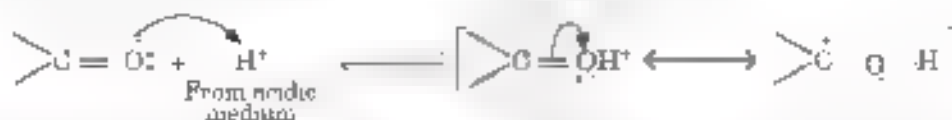


Fig. 2. Nucleophilic attack on carbonyl carbon

If the attacking nucleophiles are weak (e.g., amines and carbanion derivatives), the reaction of aldehydes and ketones are usually carried out in the weakly acidic medium. Such reactions are called **acid catalysed nucleophilic addition reactions**.

Acid catalysed addition reactions. Many reactions of carbonyl groups involve an initial protonation of the oxygen in *weakly acidic medium*. The protonation increases the positive charge of the carbonyl carbon so that it is more readily attacked by weaker nucleophiles.



The nucleophile, then attacks the protonated carbonyl group to form addition product.

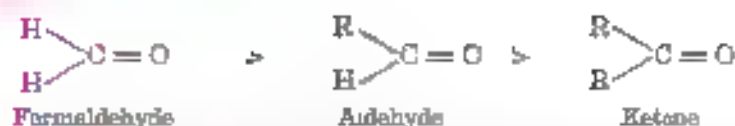


Therefore, the reactions between aldehydes and ketones and weaker nucleophiles are carried out in weakly acidic medium.

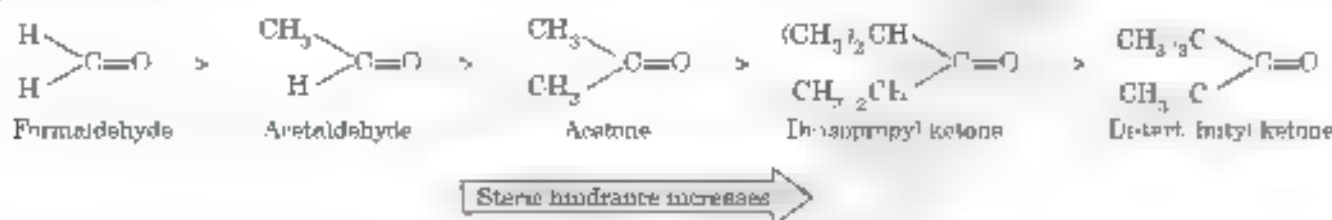
Relative Reactivity of Aldehydes and Ketones

Aldehydes and ketones readily undergo nucleophilic addition reactions. However, ketones are less reactive than aldehydes. This is due to electronic and steric effects as explained below.

1. Inductive effect The relative reactivities of aldehydes and ketones in nucleophilic addition reactions may be attributed to the amount of positive charge on the carbon. A greater positive charge means a higher reactivity. If the positive charge is dispersed throughout the molecule, the carbonyl compound becomes more stable and its reactivity decreases. Now, alkyl group is an electron-releasing group (+I inductive effect). Therefore, electron-releasing power of two alkyl groups in ketones is more than that of one in aldehyde. As a result, the electron deficiency of carbon atom (electrophilicity) in the carbonyl group is satisfied more in ketones than in aldehydes. Therefore, the reduced positive charge on carbon in case of ketones discourages the attack of nucleophiles. Hence, electron-rich ketones are less reactive than aldehydes. **Formaldehyde with no alkyl group is the most reactive of the aldehydes and ketones.** Thus, the order of reactivity is

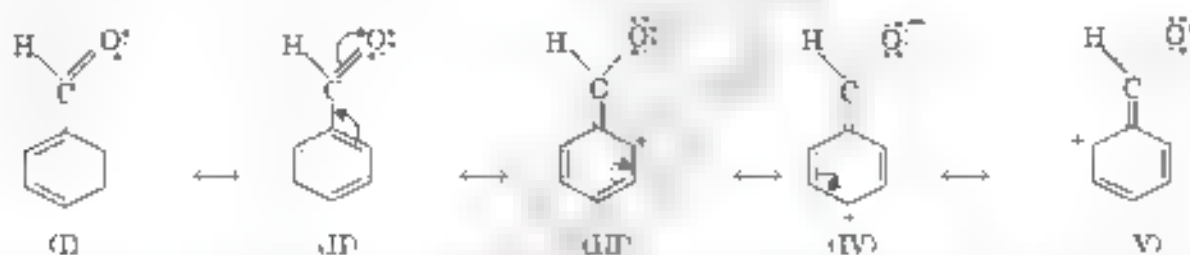


2. Steric effect. The size of the alkyl group is more than that of hydrogen. In aldehydes, there is one alkyl group but in ketones, there are two alkyl groups attached to the carbonyl group. The alkyl groups are larger than a hydrogen atom and these cause hindrance to the attacking group. This is called **steric hindrance**. As the number and size of the alkyl groups increases, the hindrance to the attack of nucleophile also increases and reactivity decreases. The lack of hindrance to nucleophilic attack is another reason for the greater reactivity of formaldehyde. Thus, the reactivity follows the order

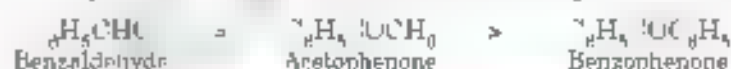


Aromatic Aldehydes and Ketones

In general, **aromatic aldehydes and ketones** are less reactive than the corresponding aliphatic analogues. For example, benzaldehyde is less reactive than aliphatic aldehydes. This can be easily understood from the resonating structures of benzaldehyde as shown below



It is clear from the resonating structures that due to electron-releasing +I effect of the benzene ring, the magnitude of the positive charge on the carbonyl group decreases and consequently it becomes less susceptible to the nucleophilic attack. Thus, aromatic aldehydes and ketones are less reactive than the corresponding aliphatic aldehydes and ketones. However, amongst aromatic aldehydes and ketones, aromatic aldehydes are more reactive than alkyl aryl ketones which in turn are more reactive than diaryl ketones. Thus, the order of reactivity of aromatic aldehydes and ketones is



SOLVED EXAMPLES

Example 6.

Arrange the following carbonyl compounds in the increasing order of their reactivity in nucleophilic addition reactions

(i) Ethanal, propanal, propanone, butanone

(ii) Benzaldehyde, *p*-tolualdehyde, *p*-nitrobenzaldehyde, acetophenone

Tripart S.B. 20.8

Solution

The electron-donating inductive effect and steric crowding around carbonyl group increases in the given order. Therefore, the reactivity decreases in the order



(ii) Amongst these acetophenone is ketone and therefore it is least reactive. *p*-Tolualdehyde has an electron-releasing $-\text{CH}_3$ group at the para position of the benzene ring whereas *p*-nitrobenzaldehyde has electron-withdrawing $-\text{NO}_2$ group at para position. Therefore *p*-tolualdehyde is less reactive and *p*-nitrobenzaldehyde is more reactive than benzaldehyde. Thus, the order is

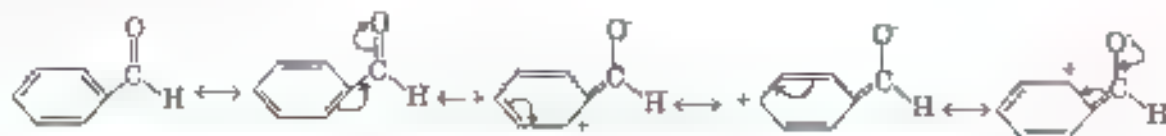


Example 7.

Would you expect benzaldehyde to be less or more reactive in nucleophilic addition than propanal? Explain.

[N.C.E.R.T.]

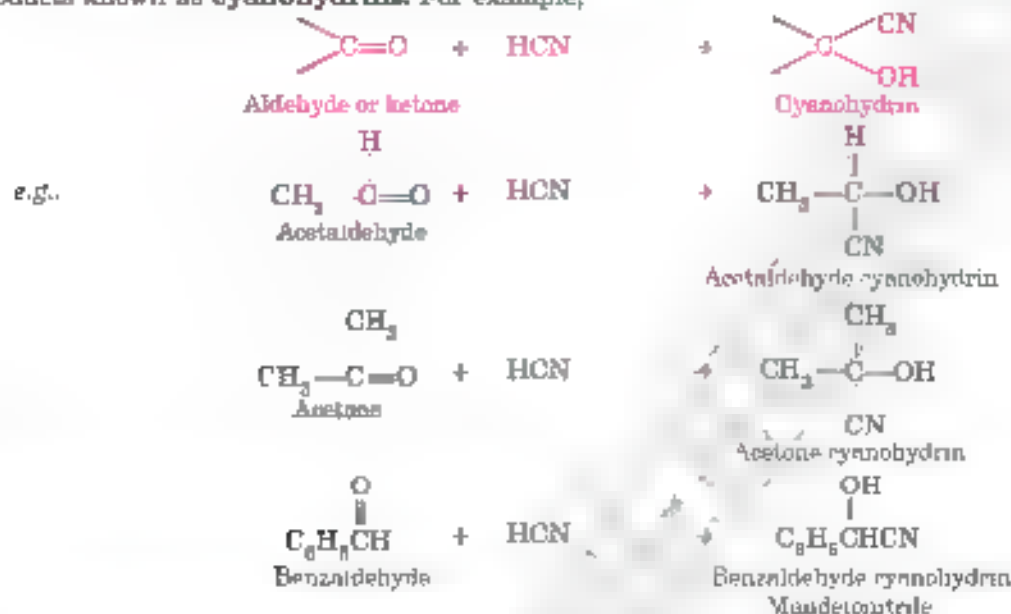
Solution: The carbon atom of the carbonyl group of benzaldehyde is less electrophilic than carbon atom of the carbonyl group in the propanal. This is because the polarity of the carbonyl group is decreased in benzaldehyde due to resonance. Therefore, benzaldehyde is less reactive than propanal.



SOME IMPORTANT EXAMPLES OF NUCLEOPHILIC ADDITION REACTIONS

Some important nucleophilic addition reactions of aldehydes and ketones are given below:

1. Addition of hydrogen cyanide. Both aldehydes and ketones react with hydrogen cyanide to form addition products known as cyanohydrins. For example,

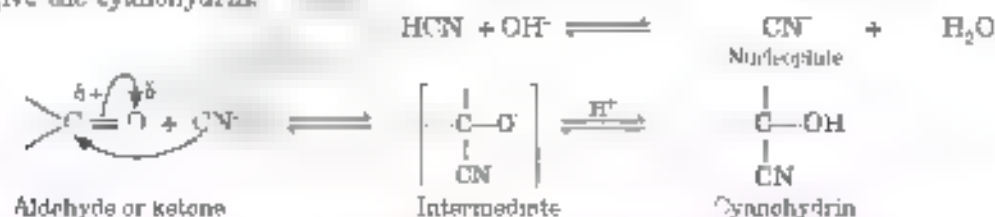


It may be noted that the reaction occurs very slowly with pure HCN. Therefore, the reaction is carried out in the presence of a base which acts as a catalyst. The base removes a proton from hydrogen cyanide and thereby produces CN^- ions and makes the reaction fast.

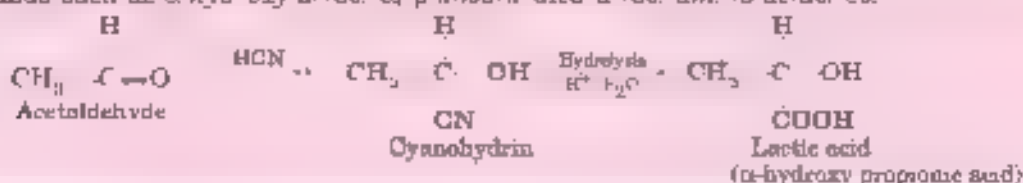


In actual practice, HCN needed for the purpose is produced *in situ* by the action of dilute mineral acid on sodium cyanide.

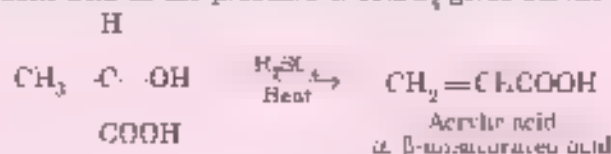
The reaction is believed to proceed as follows. The positively polarised carbon of carbonyl group is attacked by strongly nucleophilic CN^- with the simultaneous transfer of π -electrons to oxygen. The oxygen then combines with H^+ to give the cyanohydrin.



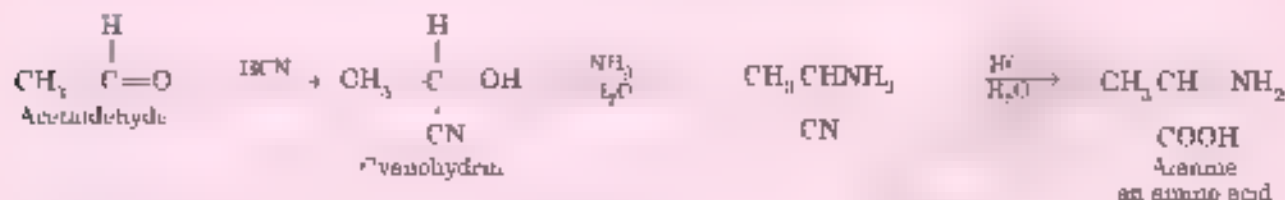
Cyanohydrins are **useful compounds** in organic synthesis. These can be used to prepare many other organic compounds such as α -hydroxy acids, α , β -unsaturated acids, amino acids, etc.



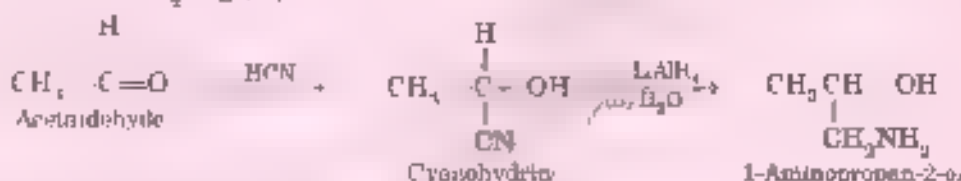
On subsequent heating lactic acid in the presence of H_2SO_4 gives acrylic acid (α, β -unsaturated acid).



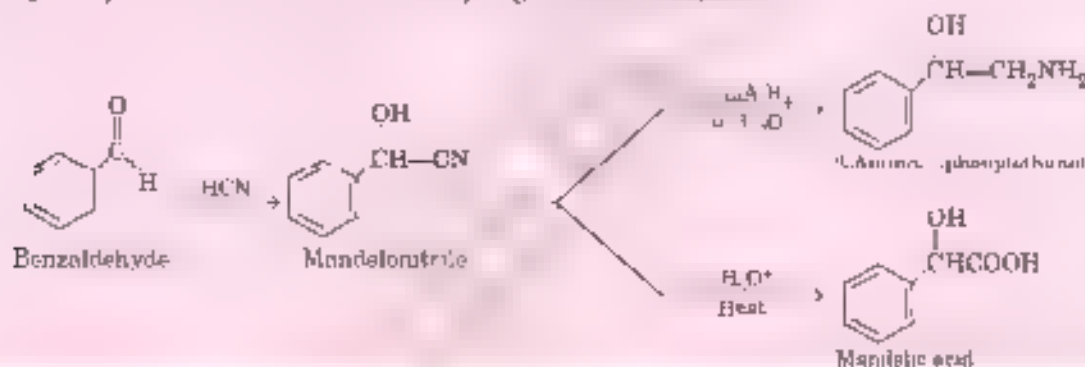
Cyanohydrins can also be converted into amino acids.



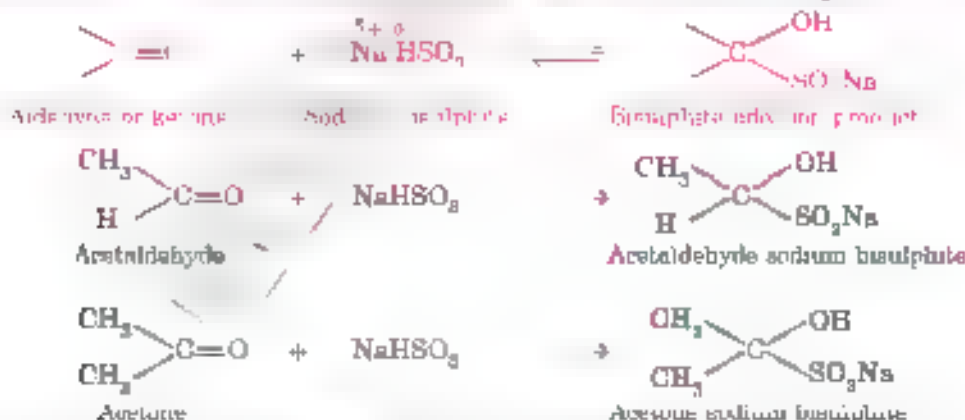
Cyanohydrin can be reduced with LiAlH_4 to give β -amino alcohols



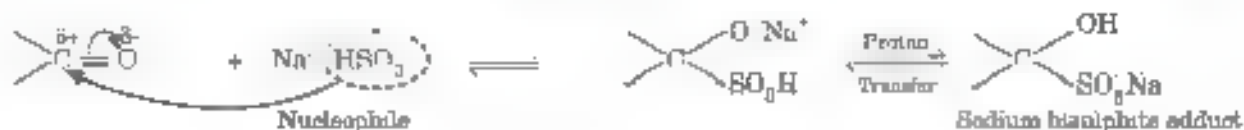
Similarly cyanohydrin formation of benzaldehyde gives different products



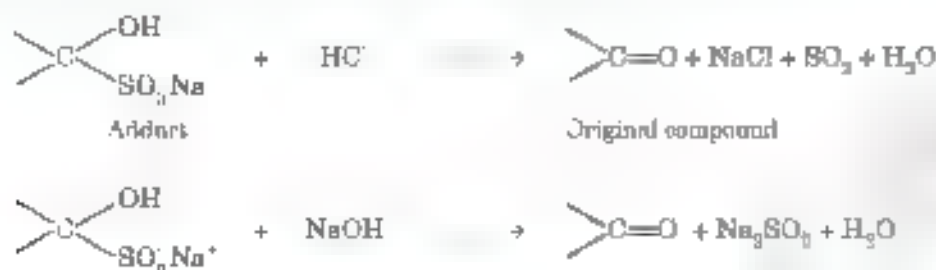
2. Addition of sodium bisulphite. Both aldehydes and ketones form *crystalline addition compounds* called **bisulphite adducts** when treated with a saturated solution of sodium bisulphite. For example



The reaction involves the nucleophilic attack of bisulphite (HSO_3^-) on the polarised carbonyl carbon atom followed by proton transfer and combination with Na^+ ion as:



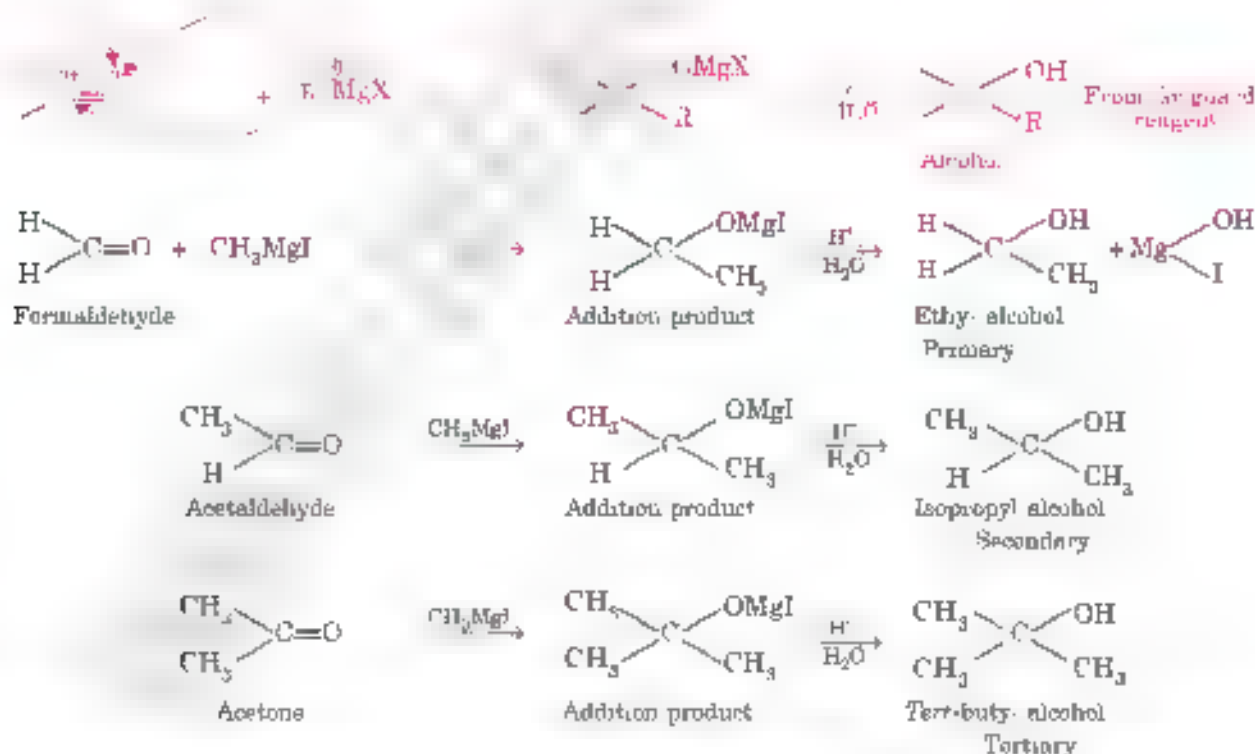
It may be noted that the position of equilibrium lies largely to the right for most aldehydes and to the left for most ketones due to steric reasons. The α -sulphur addition products of aldehydes and ketones are crystalline solids and are water soluble. As the reaction is reversible, the addition products can be decomposed by mineral acids or aqueous alkalis to give back the original aldehyde or ketone. Therefore, the reaction can be used in the purification and separation of aldehydes and ketones from other non-carbonyl compounds.



It may be noted that the compounds such as diethyl ketone, acetophenone, benzophenone, etc. do not undergo this reaction. This may be probably due to the steric hindrance of the bulky groups present around the carbonyl group.

8. Reaction with Grignard reagents (RMgX). Aldehydes and ketones react with Grignard reagents to form addition products. When the addition product is hydrolysed by water, it gives alcohols.

Formaldehyde produces primary alcohols, other aldehydes give secondary alcohols, while ketones give tertiary alcohols as illustrated below.



The reaction is believed to proceed by the nucleophilic attack of R⁻ anion on the positively charged carbon of the carbonyl group.



In these reactions, the alkyl or aryl group of the Grignard reagent is transferred to the carbon atom of the carbonyl group.

R^{MgX} Grignard reagent

- $\xrightarrow{\text{HCHO}}$
 $\begin{array}{c} \text{OMgX} \\ | \\ \text{H}-\text{C}-\text{H} \\ | \\ \text{R} \end{array} \xrightarrow{\text{H}^+ \text{H}_2\text{O}} \begin{array}{c} \text{OH} \\ | \\ \text{H}-\text{C}-\text{H} \\ | \\ \text{R} \end{array} \quad \text{1}^\circ \text{ alcohol}$
- $\xrightarrow{\text{R}^{\text{HCHO}}}$
 $\begin{array}{c} \text{OMgX} \\ | \\ \text{R}-\text{C}-\text{H} \\ | \\ \text{R} \end{array} \xrightarrow{\text{H}^+ \text{H}_2\text{O}} \begin{array}{c} \text{OH} \\ | \\ \text{R}-\text{C}-\text{H} \\ | \\ \text{R} \end{array} \quad \text{2}^\circ \text{ alcohol}$
- $\xrightarrow{\text{R}^{\text{O}}-\text{C}-\text{R}^{\text{R}}}$
 $\begin{array}{c} \text{OMgX} \\ | \\ \text{R}-\text{C}-\text{R}^{\text{R}} \\ | \\ \text{R} \end{array} \xrightarrow{\text{H}^+ \text{H}_2\text{O}} \begin{array}{c} \text{OH} \\ | \\ \text{R}-\text{C}-\text{R}^{\text{R}} \\ | \\ \text{R} \end{array} \quad \text{3}^\circ \text{ alcohol}$

$$\begin{array}{ccc}
 \begin{array}{c} \text{CH}_3 \\ \diagdown \\ \text{C}=\text{O} \\ \diagup \\ \text{CH}_3 \end{array} & + & \begin{array}{c} \text{H}-\text{O}-\text{CH}_2 \\ | \\ \text{H}-\text{O}-\text{CH}_2 \end{array} \\
 \text{Acetone} & & \text{Ethylene glycol}
 \end{array}
 \xrightarrow[\text{225}]{\text{Dry HCl}}
 \begin{array}{c} \text{CH}_3 \\ \diagdown \\ \text{C} \begin{array}{l} \diagup \text{O}-\text{CH}_2 \\ \diagdown \text{O}-\text{CH}_2 \end{array} \\ \diagup \\ \text{CH}_3 \end{array}$$

Cyclic ketal.
Ethylene glycol ketal).

The above reactions are reversible. Therefore, the acetals and ketals are hydrolysed with aqueous mineral acids to regenerate the aldehydes and ketones.



B. Nucleophilic Addition Reactions followed by Loss of Water

5. Addition of ammonia derivatives. Aldehydes and ketones react with a number of ammonia derivatives $\text{H}_2\text{N}-\text{Z}$ in weakly acidic medium to form compounds containing carbon-nitrogen double bonds with the elimination of water molecule. The reaction is reversible and is catalysed by acid. The equilibrium favours the product formation due to the rapid dehydration of the intermediate to form $\text{C}=\text{N}-\text{Z}$. For example



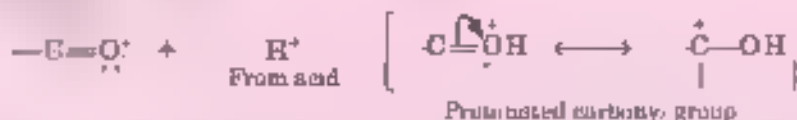
Some of these compounds are crystalline and are used for the characterization of aldehydes and ketones. The common ammonia derivatives and the products formed are given below.

Ammonia derivative	Group Z	Product with RCHO
NH_2OH Hydroxylamine	-OH	$\text{RCH}=\text{N}\cdot\text{OH}$ Oxime
NH_2NH_2 Hydrazine	$-\text{NH}_2$	$\text{RCH}=\text{N}\cdot\text{NH}_2$ Hydrazone
NH_2NHPh Phenyl hydrazine	$\text{NH}-\text{C}_6\text{H}_5$	$\text{RCH}=\text{N}\cdot\text{NH}-\text{C}_6\text{H}_5$ Phenyl hydrazone
$\text{NH}_2\text{NH}-\text{C}_6\text{H}_3(\text{NO}_2)_2$ 2,4-Dinitrophenyl hydrazine	$\text{NH}-\text{C}_6\text{H}_3(\text{NO}_2)_2$	$\text{RCH}=\text{N}\cdot\text{NH}-\text{C}_6\text{H}_3(\text{NO}_2)_2$ 2,4-Dinitrophenyl hydrazone
$\text{NH}_2\text{NHCONH}_2$ Semicarbazide	NHCONH_2	$\text{RCH}=\text{N}\cdot\text{NHCONH}_2$ Semicarbazone

Experiment 12: Control pH using addition of ammonia derivatives to aldehydes and ketones

The ammonia derivatives contain lone pair of electrons and therefore their reaction with aldehydes and ketones involves the nucleophilic attack by the basic nitrogen compound on the carbonyl carbon. The ammonia derivatives are weak nucleophiles and therefore the reaction is catalysed by weakly acidic medium. The reaction occurs in the steps given below.

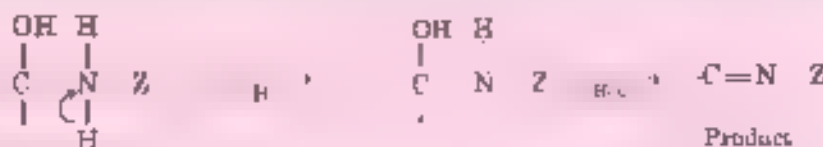
Step I. In acidic medium carbonyl oxygen gets protonated



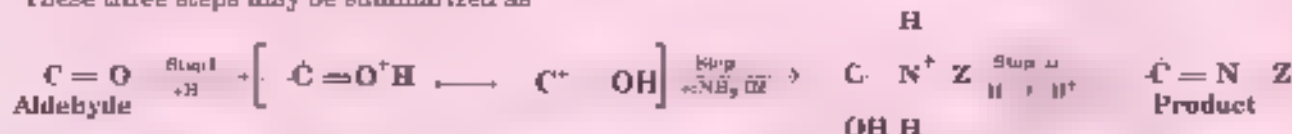
Step II. The ammonia derivatives in which the nitrogen atom has a lone pair of electrons act as nucleophiles and attack the positively charged carbonyl carbon. The formation of carbon-nitrogen bond results a positive charge on nitrogen atom.



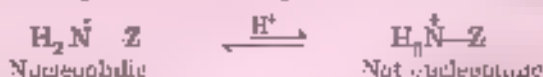
Step I.] The intermediate formed in step II is unstable which loses a proton H^+ and water molecule to form a stable product.



These three steps may be summarized as



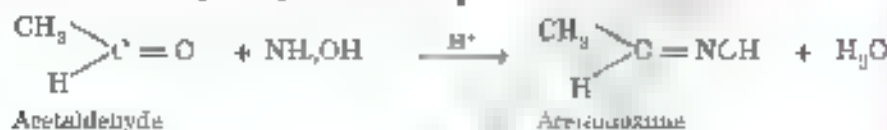
Therefore it is observed that the protonation of carbonyl oxygen makes the carbonyl carbon more susceptible to nucleophilic attack and, therefore, we expect that the reaction will be favoured by high acidic medium. However the medium should not be **highly acidic**. This is because if the medium is highly acidic, then the ammonia derivatives being basic in nature, may form their respective ammonium salts N^+H_4X .



These salts of ammonia derivatives cannot act as nucleophiles because of the lack of unshared electron pair. Therefore, the reaction does not occur. Thus, to carry out these reactions we have to control the acidity (strength) of the medium i.e. pH. The optimum pH of the medium should be between 3 and 4.

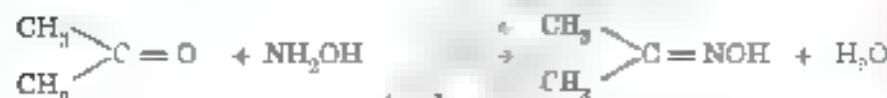
Some of these reactions are discussed below

i. Reaction with hydroxylamine (NH_2OH) to form oximes



Acetaldehyde

Acetoxime
Ethanal oxime.



Acetone

Acetoxime
Propanone oxime



Reaction with hydrazine (NH_2-NH_2) to form hydrazone



Acetaldehyde

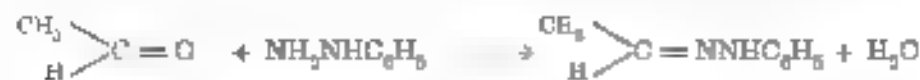
Acetaldehyde hydrazone
Ethanal hydrazone



Acetone

Acetone hydrazone
Propanone hydrazone

ii. Reaction with phenylhydrazine ($C_6H_5NHNH_2$) to give phenylhydrazone.



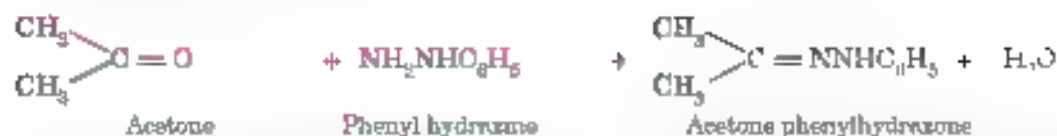
Acetaldehyde

Phenylhydrazine

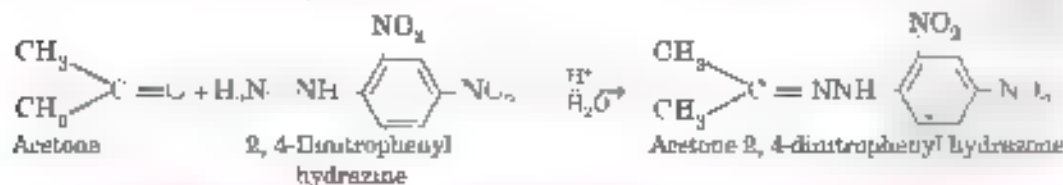
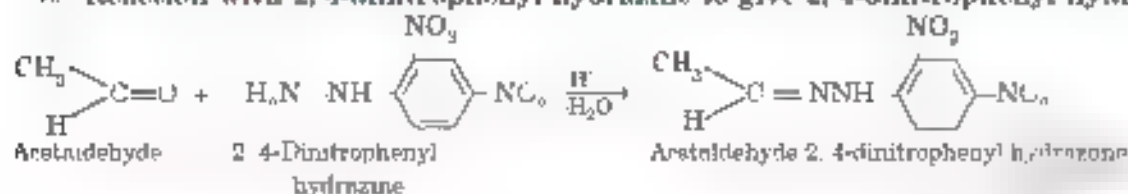
Acetaldehyde phenylhydrazone
Ethanal phenylhydrazone

NOTE

The reactions of aldehydes and ketones with ammonia derivatives give characteristic solids (e.g. sharp melting points) which are often used for the characterisation of these compounds.

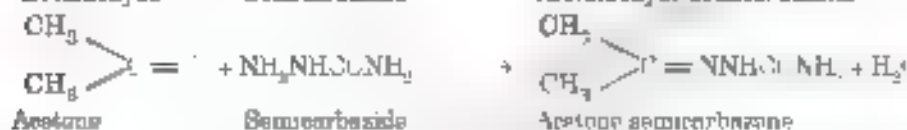


2c. Reaction with 2, 4-dinitrophenyl hydrazine to give 2, 4-dinitrophenyl hydrazone.



These products are yellow or orange or red coloured crystalline compounds called DNP derivatives and can be used for the identification of aldehydes and ketones.

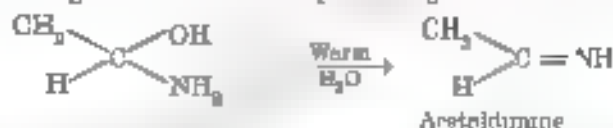
c. Reaction with semicarbazide ($\text{NH}_2\text{NHC(=O)NH}_2$) to give semicarbazone



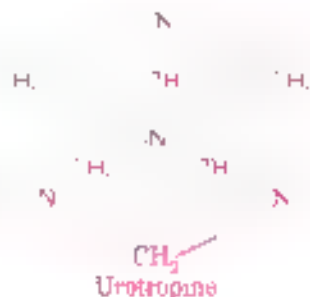
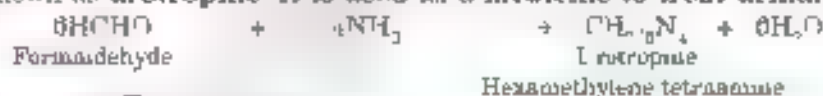
Reaction with ammonia. Aldehydes (except formic aldehyde) react with ammonia to form cyclic (see ammonia adducts).



The adduct on warming with water decomposes to give an imino-



Formaldehyde reacts with ammonia to form hexamethylenetetramine, $\text{CH}_2)_6\text{N}_4$, which is also known as urotropine. It is used as a medicine to treat urinary infections.

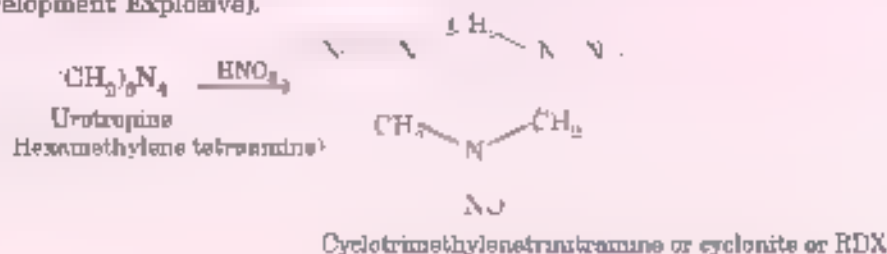


Are You Curious...

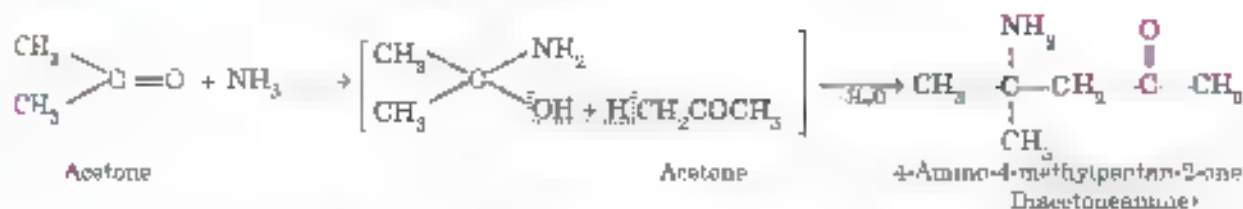


□ RDX has many civilian and military applications. What is RDX?

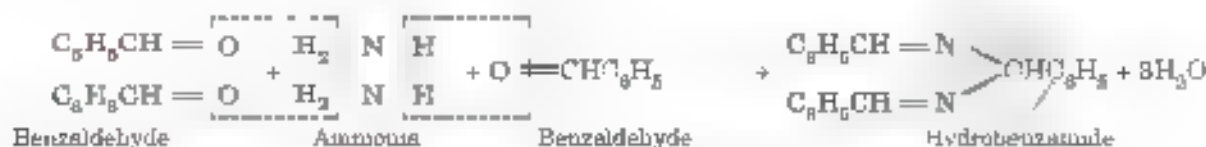
► Nitration of nitrobenzene under controlled conditions gives the well known explosive compound RDX (Research and Development Explosive).



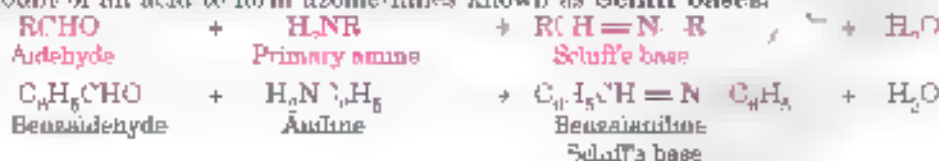
Acetone reacts with ammonia to form diacetone amine.



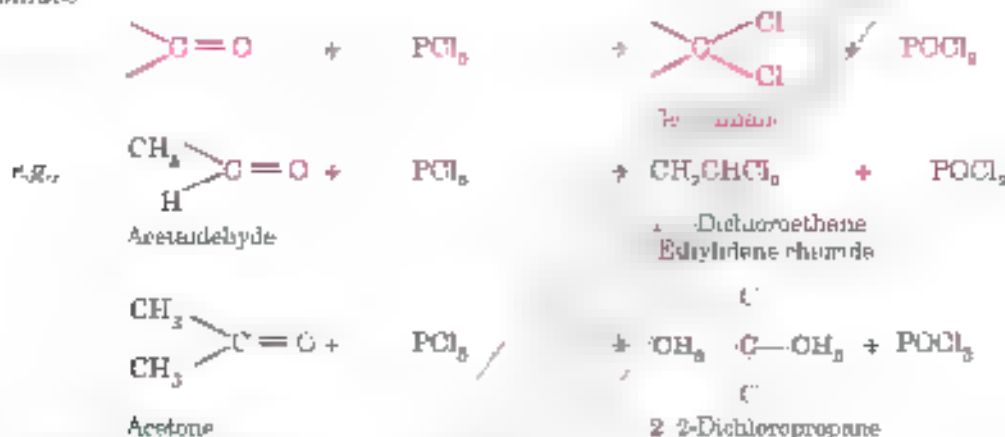
Benzaldehyde reacts with ammonia to form hydrobenzamide



7. Reaction with primary amines. Aldehydes and ketones react with primary amines in the presence of a catalytic amount of an acid to form azomethanes known as **Schiff bases**.



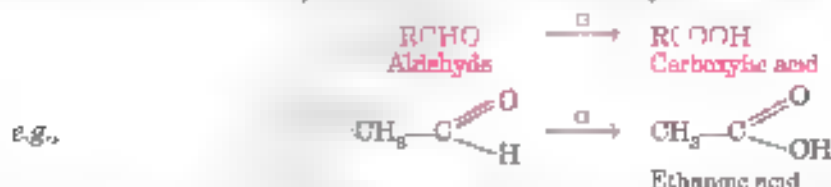
8. Reaction with phosphorus pentachloride. When aldehydes or ketones react with PCl_5 , they form gem. dihalides



C. Oxidation Reactions

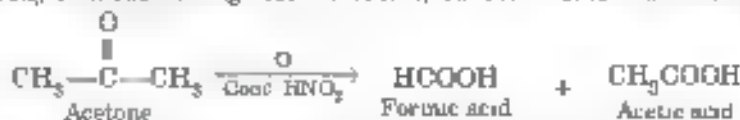
9. Oxidation of aldehydes and ketones

a. Aldehydes differ from ketones in their oxidation reactions. Aldehydes can be easily oxidised to carboxylic acids on treatment with common oxidising agents like nitric acid, KMnO_4 , $\text{K}_2\text{Cr}_2\text{O}_7$, etc. The carboxylic acids formed contain the same number of carbon atoms as the aldehyde.



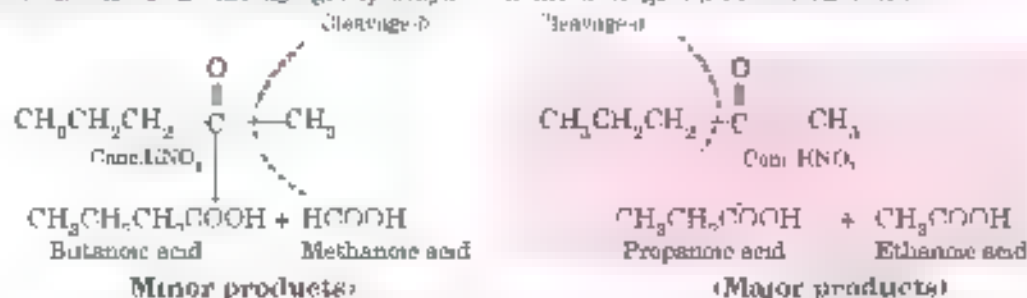
The reason for the easy oxidation of aldehyde is the presence of a hydrogen atom on the carbonyl group which can be converted into $-\text{OH}$ group without undergoing the cleavage of any other bond.

Ketones are not easily oxidised. However, under drastic conditions i.e. with powerful oxidising agents such as conc. HNO_3 , $\text{KMnO}_4/\text{H}_2\text{SO}_4$ or $\text{K}_2\text{Cr}_2\text{O}_7/\text{H}_2\text{SO}_4$ at elevated temperatures, ketones undergo cleavage of carbon-carbon bond giving a mixture of carboxylic acids having less number of carbon atoms than the original ketone.



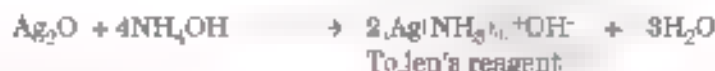
In case of unsymmetrical ketones, the cleavage occurs in such a way that keto group stays preferentially with the smaller alkyl group. This is known as **Pinacol's rule**. For example in the oxidation of pentan-2-one the major

mode of cleavage is α' , in which the methyl group stays with the keto group as shown below



This oxidation reaction can be used to distinguish between aldehydes and ketones. The basis of this test is that aldehydes are very readily oxidised not only by strong oxidising agents like KMnO_4 , $\text{K}_2\text{Cr}_2\text{O}_7$ etc. but also by weak oxidising agents like **Tollen's reagent**, **Fehling's solution**, **Benedict's solution** etc. Under these conditions, ketones are not oxidised by these reagents. Therefore, these tests can be used to distinguish aldehydes or ketones.

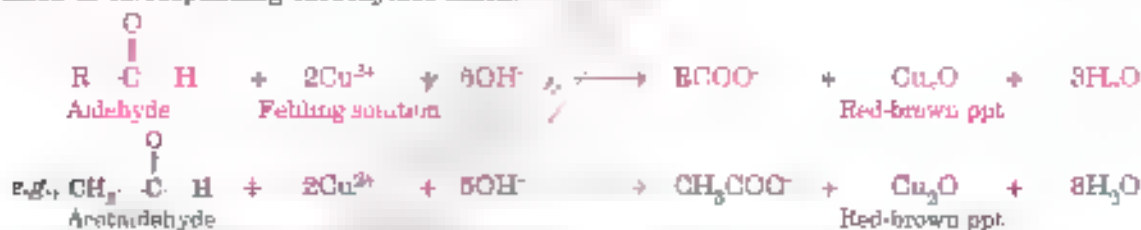
Tollen's reagent. Tollen's reagent is ammoniacal solution of AgNO_3 . It is prepared by adding NH_4OH solution to AgNO_3 solution till the precipitates of Ag_2O first formed just gets dissolved. It has the formula $\text{Ag}(\text{NH}_3)_2^+ \text{OH}^-$. When an aldehyde is heated with Tollen's reagent, the aldehyde reduces it, i.e., it is oxidised to metallic silver and a bright silver mirror is produced on the inner side of the test tube. The aldehyde is oxidised to corresponding carboxylate anion.



This reaction is also known as **silver mirror test**. The **silver mirror** formed indicates the presence of aldehydic group in the molecule.

Both aliphatic and aromatic aldehydes reduce Follen's reagent. Ketones do not give this test.

ii) Fehling's solution. Fehling reagent contains two solutions, Fehling solution A and Fehling solution B. Fehling solution A is an aqueous solution of copper sulphate and Fehling solution B is alkaline solution of sodium potassium tartarate (Rochelle salt). These two solutions are mixed in equal amounts before test. When an aldehyde is heated with Fehling solution, a reddish brown precipitate of cuprous oxide (Cu_2O) is formed. Aldehydes are oxidised to corresponding carboxylate anion.

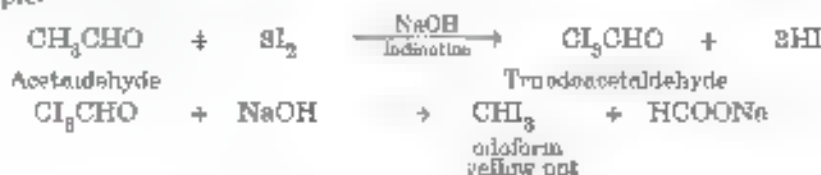


Aromatic aldehydes, however, do not respond to this test.

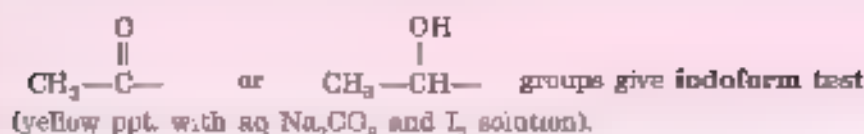
Ketones also do not give this test.

1. **Benedict's solution.** This is an alkaline solution of cupric Cu^{2+} ion complexed with citrate ions. It reacts in the same way as the Fehling solution.

(b) **Oxidation with sodium hypohalite + Haloform reaction.** Aldehydes and ketones having at least one methyl group: linked to the carbonyl carbon atom; e. methyl ketones CH_3COR and acetyl benzyde are easily oxidised by excess of halogen in the presence of alkali Cl_2 , Br_2 , I_2 in the presence of dil NaOH or sodium hypohalite NaOX to give haloform (chloroform, bromoform or iodoform). For example, when the reaction is carried out with sodium hypohalite NaOI ($\text{Cl}_2 + \text{aq. NaOH}$) a yellow ppt. of iodoform is produced. This reaction is also known as **haloform reaction**. For example,



- Remember. The compounds containing



Therefore, iodoform test helps to distinguish between :

I O D O F O R M T E S T	Carbonyl compounds ($\text{CH}_3-\overset{\text{O}}{\underset{\text{ }}{\text{C}}}-$)	
	☐ Methanal (HCHO) and ethanal (CH_3CHO)	
	▪ Ethanal gives this test	
	☐ Ethanal (CH_3CHO) and propanal ($\text{CH}_3\text{CH}_2\text{CHO}$)	
	▪ Ethanal gives this test	
	☐ Pentan-2-one ($\text{H}_3\text{CC}-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$) and pentan-3-one ($\text{CH}_3\text{CH}_2\text{COCH}_2\text{CH}_3$)	
	▪ Pentan-2-one gives this test	
	☐ Acetophenone ($\text{C}_6\text{H}_5\text{COCH}_3$) and benzophenone ($\text{C}_6\text{H}_5\text{COC}_6\text{H}_5$)	
	▪ Acetophenone gives this test	
	☐ Benzaldehyde ($\text{C}_6\text{H}_5\text{CHO}$) and acetophenone ($\text{C}_6\text{H}_5\text{COCH}_3$)	
	▪ Acetophenone gives this test	
Alcohols ($\text{CH}_3-\overset{\text{OH}}{\underset{ }{\text{CH}}}-$)		
☐ Ethanol ($\text{CH}_3\text{CH}_2\text{OH}$) and methyl (CH_3CH)		
▪ Ethanol gives this test		
☐ Ethanol ($\text{CH}_3\text{CH}_2\text{OH}$) and propanol ($\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$)		
▪ Ethanol gives this test		
☐ Propan-2-ol ($\text{CH}_3\text{CH}(\text{OH})\text{CH}_3$) and propan-1-ol ($\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$)		
▪ Propan-2-ol gives this test		
☐ Butan-2-ol ($\text{CH}_3\text{CH}(\text{OH})\text{CH}_2\text{CH}_3$) and butan-1-ol ($\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$)		
▪ Butan-2-ol gives this test		

D. Reduction of Aldehydes and Ketones

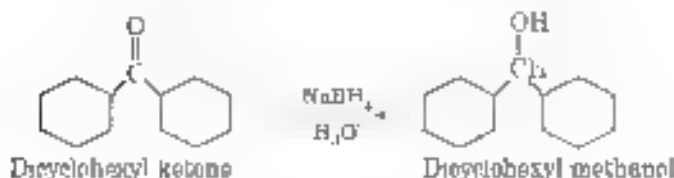
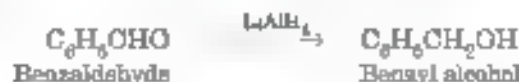
10. Reduction of aldehydes and ketones. Aldehydes and ketones are reduced to a variety of compounds under different conditions.

1. Reduction to alcohols

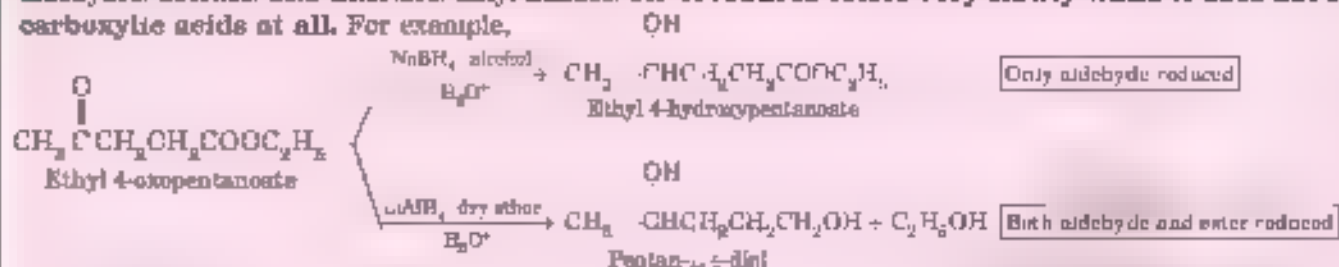
Aldehydes and ketones on catalytic hydrogenation in the presence of Ni, Pt or Pd or chemically by complex metal hydrides such as lithium aluminium hydride (LiAlH_4) or sodium borohydride (NaBH_3) give alcohols. Aldehydes on reduction give primary alcohols and ketones give secondary alcohols.



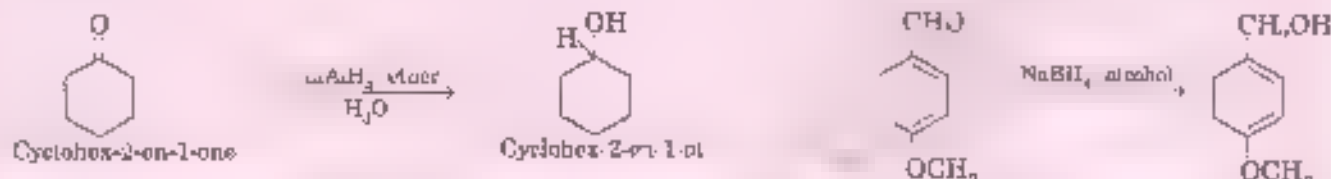
For example,



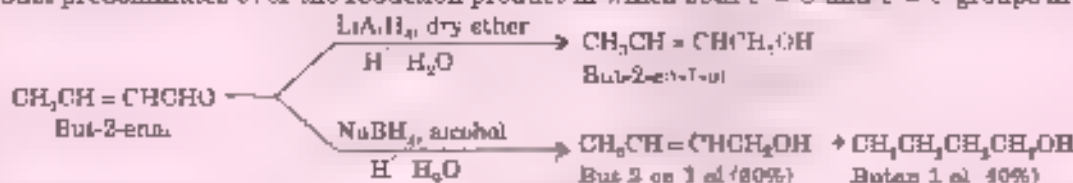
It may be noted that all the above reducing agents H_2/Ni , Pt or Pd , $LiAlH_4$ and $NaBH_4$ are very effective reducing agents. **$LiAlH_4$ is much more reactive than $NaBH_4$** . It not only reduces aldehydes and ketones but also reduces acids, acid chlorides, anhydrides, amides, esters, nitriles, oximes, etc. However $NaBH_4$ reduces only aldehydes, ketones, and chlorides, alkyl halides, etc. It reduces esters very slowly while it does not reduce carboxylic acids at all. For example,



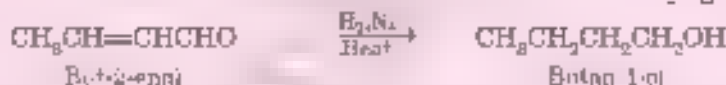
However with $LiAlH_4$ and $NaBH_4$ do not reduce isolated carbon-carbon double bonds or double bonds of benzene rings.



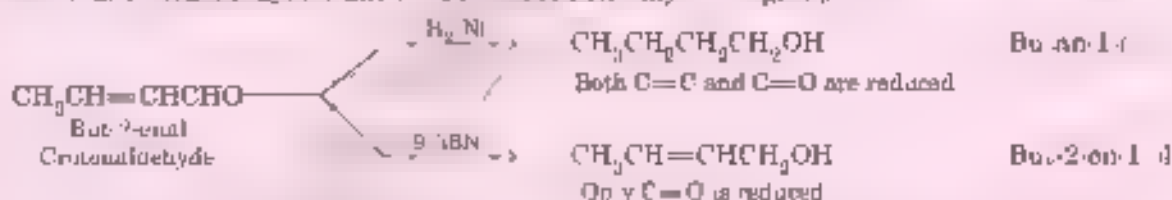
However in case of α, β unsaturated aldehydes and ketones, $LiAlH_4$ reduces only $C=O$ group leaving $C=C$ bond as such. But $NaBH_4$ reduces both the $C=C$ and $C=O$ bonds giving a mixture of products, in this $C=C$ reduction product predominates over the reduction product in which both $C=O$ and $C=C$ groups are reduced.



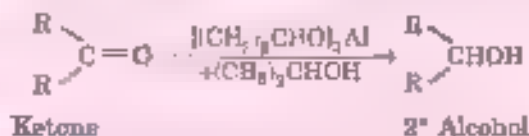
Catalytic hydrogenation can reduce both the double bond and the carbonyl group simultaneously



In order to reduce aldehyde or ketone selectively without reducing carbon-carbon double bond in the same molecule a reducing agent hydroborane known as $9-BBN$ has been suggested. This reduces the carbonyl group of unsaturated aldehydes or ketones with very high degree of selectivity. For example, H_2/Ni can reduce both $C=C$ and $C=O$ of crotonaldehyde while $9-BBN$ reduces only $C=O$ group.



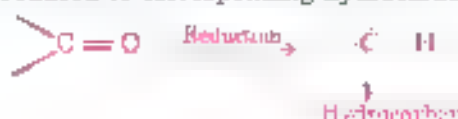
Ketones can also be reduced to corresponding secondary alcohols by treating them with aluminium isopropoxide in isopropyl alcohol.



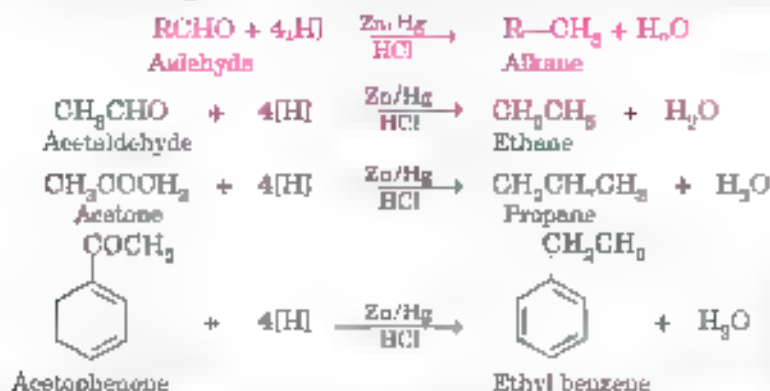
This reaction is called **Meerwein-Ponndorf-Verley reduction**. This reaction involves the transfer of a hydride ion (H^-) from isopropyl alcohol to the carbonyl carbon of ketone.

2. Reduction to hydrocarbons

Aldehydes and ketones can be reduced to corresponding hydrocarbons by the following methods



1. Reduction with zinc amalgam and conc. HCl— Clemmensen reduction

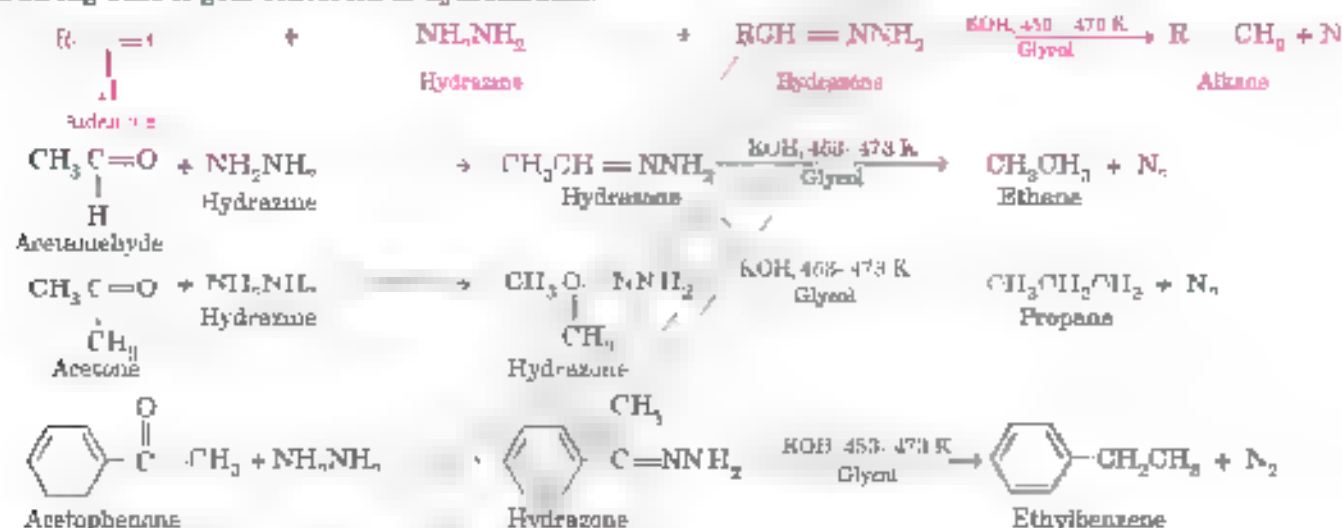


Clemmensen reduction is commonly used for aldehydes or ketones which are sensitive to alkalies.

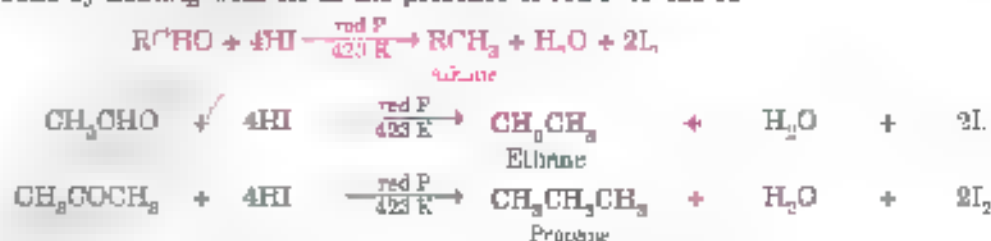
2. Reduction with basic solution of hydrazine— Wolff-Kishner reduction

In this method aldehyde or ketone is heated with a mixture of hydrazine and a strong base (KOH or potassium *tert.*-butoxide) to 453–473 K in ethylene glycol as solvent.

During this reduction, aldehyde or ketone is first converted to hydrazone with hydrazine and then in treatment with a strong base it gets converted to hydrocarbons.

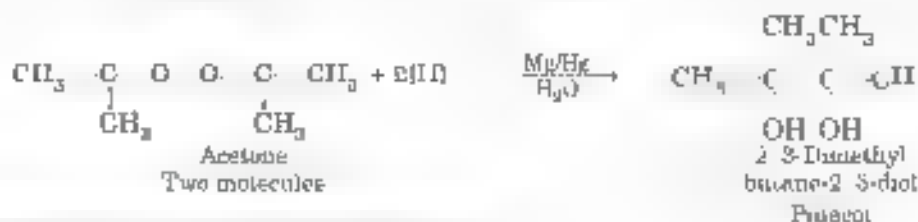


3. Reduction with HI in the presence of red phosphorus. Aldehydes and ketones are reduced to corresponding hydrocarbons by heating with HI in the presence of red P to 423 K.



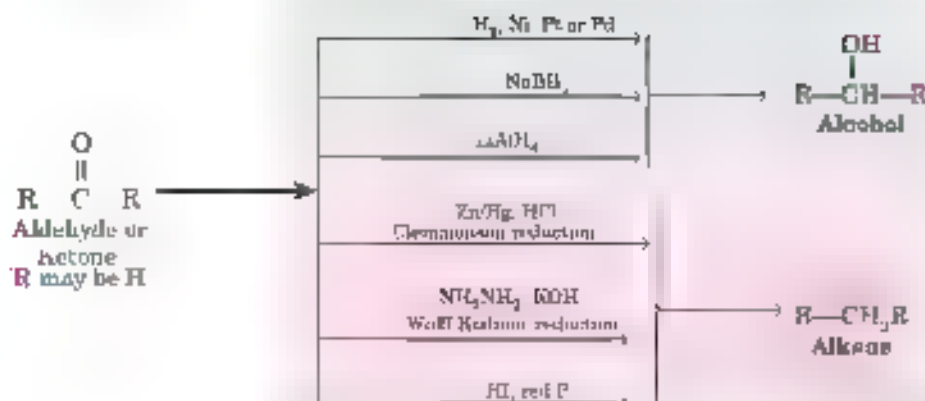
3. Reduction to pinacols (bimolecular reduction)

Ketones on reduction with magnesium amalgam and water are reduced to symmetrical diols known as **pinacols**.



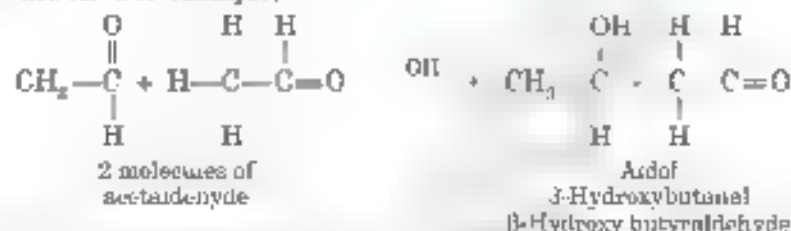
Aldehydes do not give this reaction.

Summary of reduction reactions



E. Miscellaneous Reactions

11. Aldol condensation. Aldehydes and ketones containing at least one α -hydrogen (H-atoms attached to the C-atom adjacent to the carbonyl group) undergo self condensation in the presence of dilute alkali to form β -hydroxy *aldehyde* or β -hydroxy *ketone* (ketol) respectively. This reaction is called **aldol condensation**. The word "aldol" is derived from the combination of words *aldehyde* and *alcohol* (the two functional groups present in the product **ald** + **ol** = **aldol**). For example,

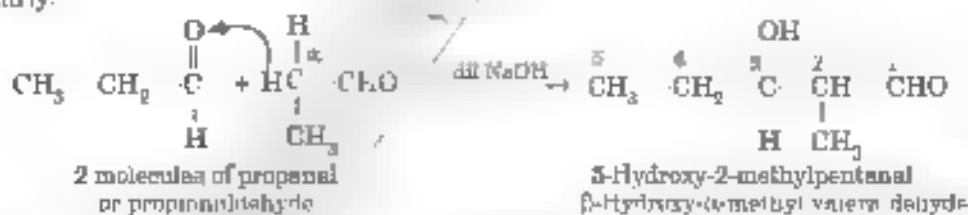


In this reaction, the product is formed in such a way that the α -carbon of one molecule becomes attached to the carbonyl carbon of the second.

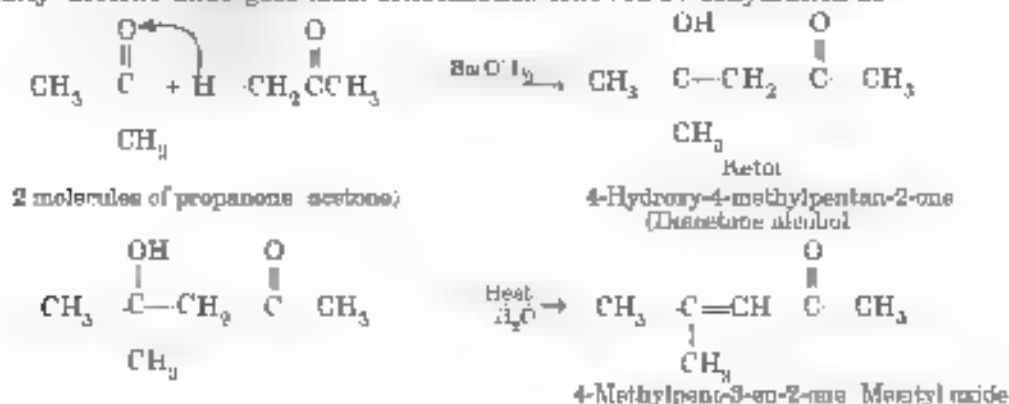
The product of aldol condensation on heating with dilute acids undergo dehydration to form α, β -unsaturated aldehydes or ketones.



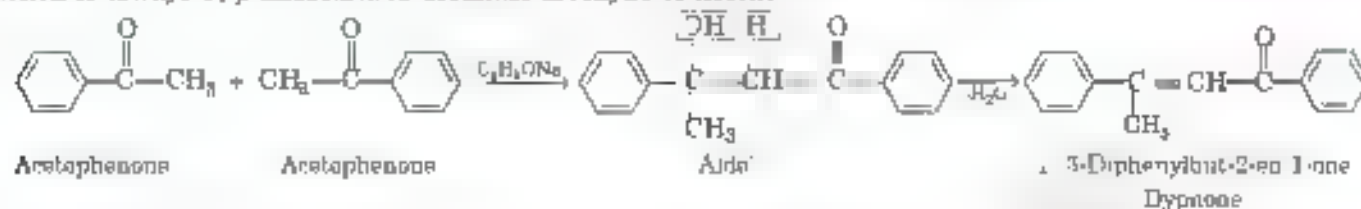
Similarly,



Similarly acetone undergoes aldol condensation followed by dehydration as



It may be noted that if carbon-carbon double bond in the product of dehydration is conjugated with aromatic ring such as benzene ring, the initially formed alcohol undergoes dehydration α to aromaticity and the product of the reaction is always α , β -unsaturated aromatic aldehyde or ketone.

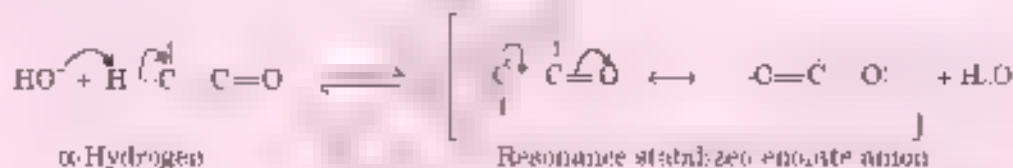


Though ketones give ketals, compounds containing a keto and alcohol groups, the general name aldol condensation still applies to the reactions of ketones due to their similarity with aldehydes.

If an aldehyde or ketone does not contain an α -hydrogen, it will not undergo aldol condensation. For example, formaldehyde $\text{H}-\text{CHO}$, benzaldehyde $\text{C}_6\text{H}_5\text{CHO}$, benzophenone $\text{C}_6\text{H}_5\text{COC}_6\text{H}_5$, etc. do not undergo aldol condensation.

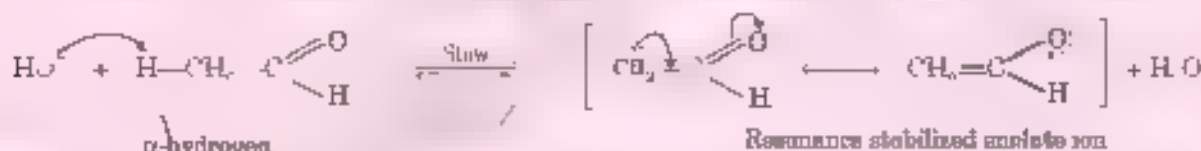
Method 2:

The α -hydrogen atoms of aldehydes and ketones are slightly acidic in nature due to strong electron withdrawing inductive $-I$ effect of the carbonyl group. This acidity of α -hydrogen is due to resonance stabilization of the conjugate base. Due to electron withdrawing inductive effect $-I$ effect of the carbonyl group, it withdraws electrons from the adjacent carbon-carbon bond. This makes α -carbon electron deficient and it in turn withdraws electron from $C_{\alpha}-H$ bond. As a result, the electron density in $C_{\alpha}-H$ bond decreases and α -hydrogens are weakly acid and therefore, can easily be abstracted by strong base as

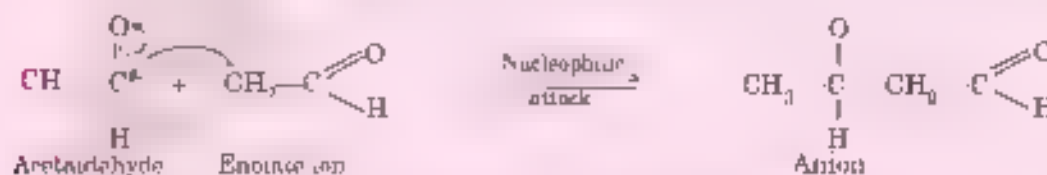


The conjugate base is called enolate anion, e.g. from double bond and *enolate* from an enolate.

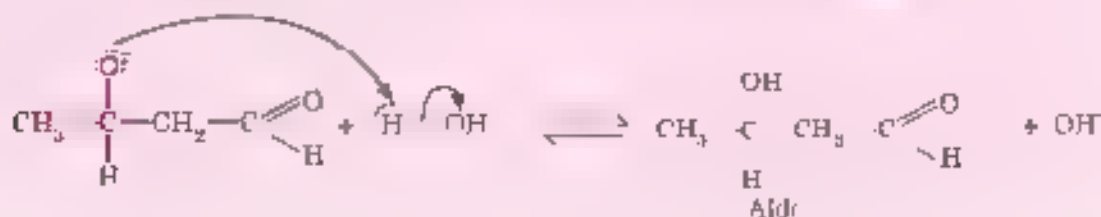
Step 1 In the first step, the base OH^- removes proton (one of the α -hydrogen atoms) to form an **enolate** ion from the aldehyde or ketone (e.g. acetaldehyde), as. The enolate is gets stabilized by resonance



Step 2. The enolate anion bearing a strong nucleophile attacks the carbonyl group of the second molecule of acetaldehyde as



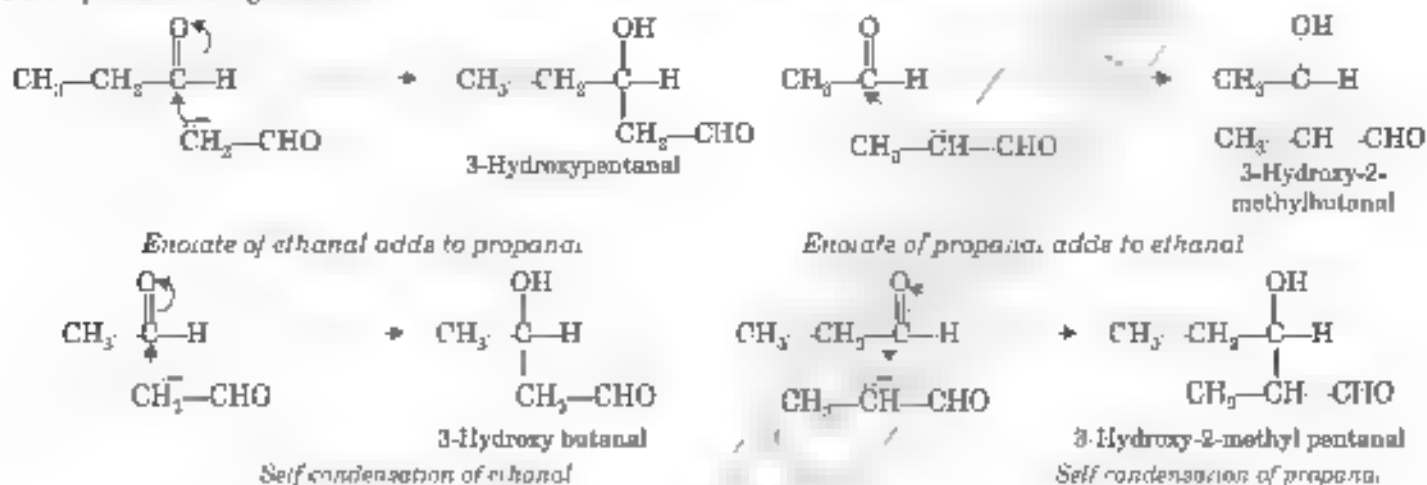
Step III The anion formed in step II abstracts a proton from water to form an alcohol



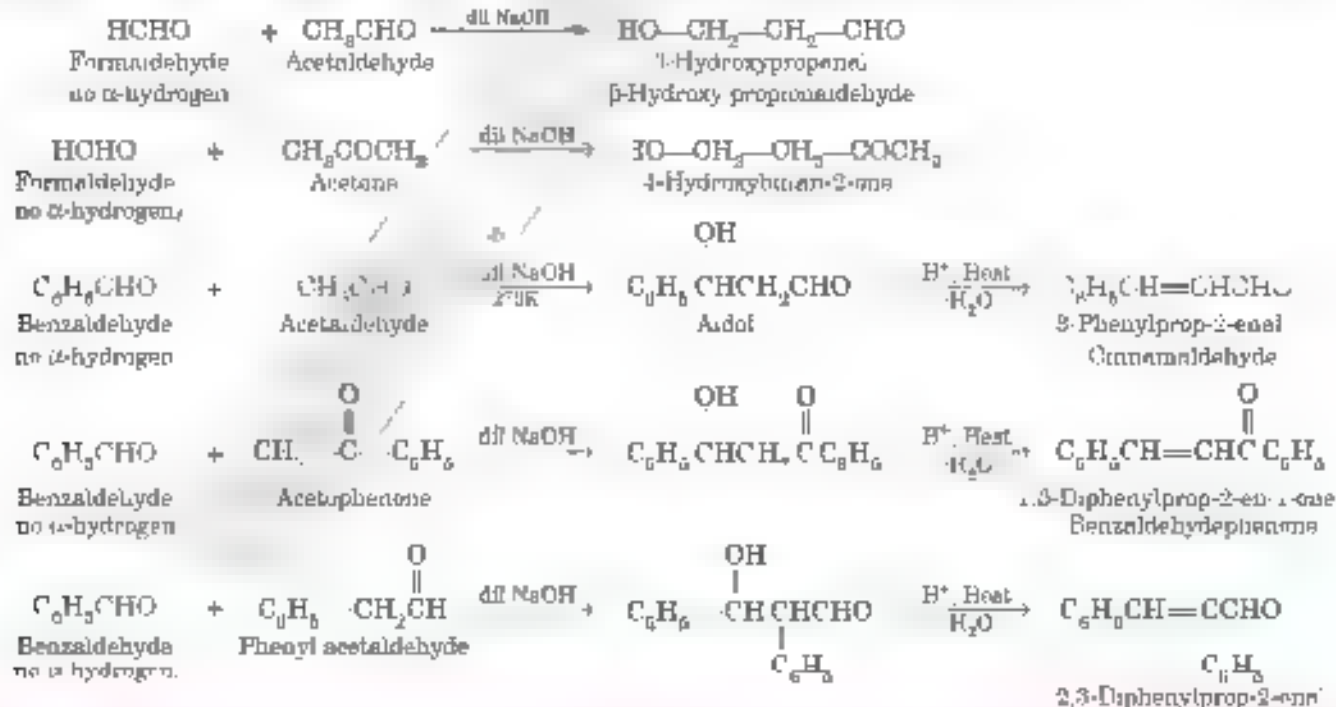
TLAB. the aldehydes or ketones which do not have α -hydrogen cannot undergo aldol condensation.

Cross aldol condensation

The aldol condensation reaction is not confined to the condensation of two molecules of the same aldehyde or ketone known as self condensation. It can also take place between two different molecules of aldehydes or ketones or between one aldehyde and one ketone. The condensation of two different carbonyl compounds in the presence of a base is called **cross aldol condensation** or **mixed condensation**. However the compound is used in these reaction must be selected carefully otherwise a mixture of several products will be formed. For example cross aldol condensation of ethanal and propanal would give four products because either of these compounds can form enolate ion. Attack by the enolate of ethanal on propanal gives a product different from the one formed by the attack of the enolate of propanal on ethanal. In addition, self condensation of ethanal and propanal also occurs. These products are given below

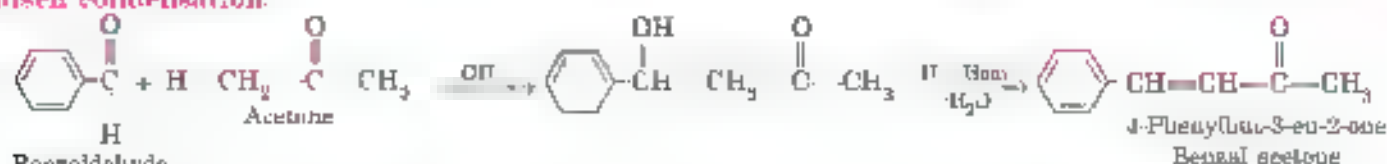


However cross aldol condensation is useful when one of the carbonyl compounds does not contain α -hydrogen and therefore can not undergo self condensation. For example methanal formaldehyde and benzaldehyde have been successfully used with other aldehydes and ketones containing α -hydrogen.



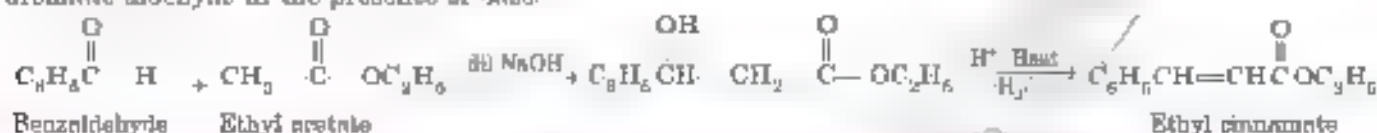
It may be noted that a cross aldol condensation can be effective if it is planned so that only one of the reactant can form an enolate ion and the other compound is more likely to react with enolate ion. The other side reaction, self condensation can be avoided by placing the compound with α -hydrogen in base and then slowly adding the reactant with no α -hydrogen to the mixture. Under these conditions the concentration of the reactant with α -hydrogen will always be low and most of it will be present as an enolate ion. Therefore, the main reaction that will take place will be between this enolate ion and that component which has no α -hydrogen.

The reaction of condensation between an aromatic aldehyde or ketone and an aliphatic aldehyde or ketone in the presence of dilute alkali to form α, β unsaturated compound is called **Claissen-Schmidt reaction** or simply **Claissen condensation**.

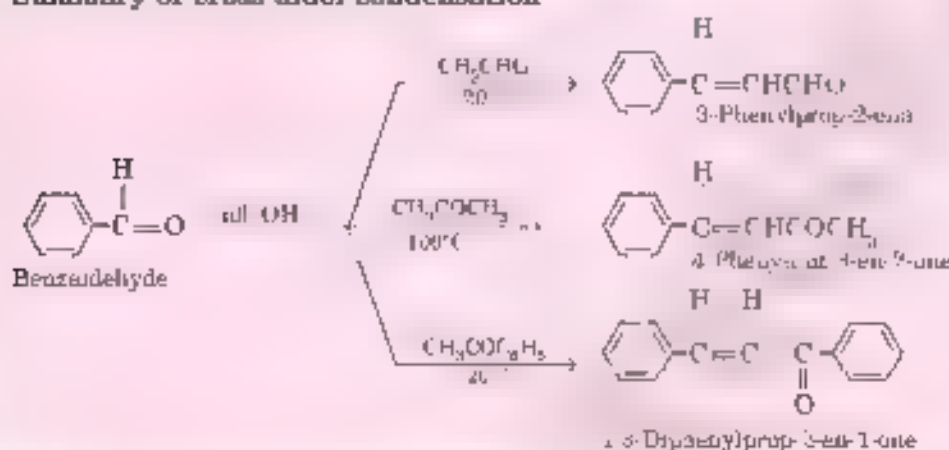


No α -hydrogen

Even aliphatic esters containing α -hydrogen atoms undergo Claissen-Schmidt condensation on treatment with an aromatic aldehyde in the presence of base.

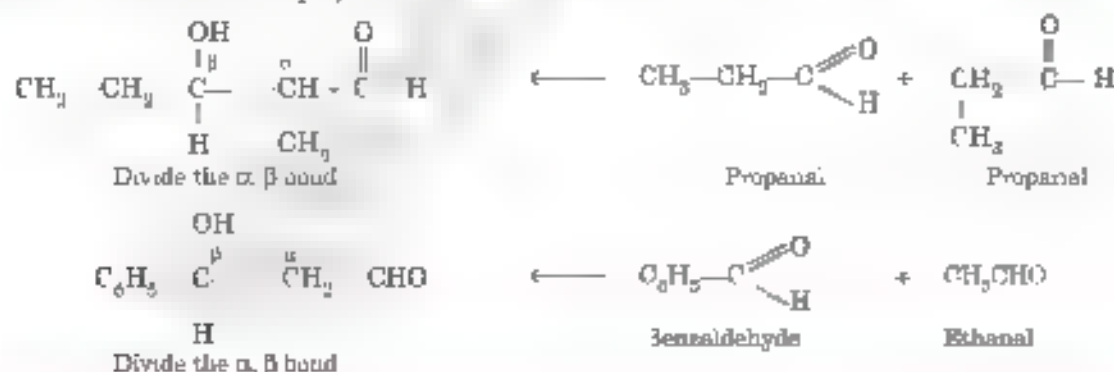


Summary of cross aldol condensation



Planning Aldol Condensation Reaction

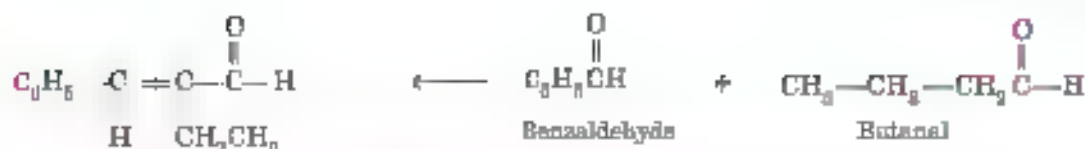
Aldol condensation reaction produces β -hydroxy aldehydes or ketones (aldols) or α, β -unsaturated aldehydes and ketones (dehydrated products). From the product required, the starting materials can be predicted. For this in case of β -hydroxy aldehydes or ketones, divide the α, β bond and in case of dehydrated product, the α, β bond is the double bond. For example,



For these, change $\text{C}-\text{OH}$ bond of β -carbon to $\text{C}=\text{O}$ and put back one H atom on the α -carbon atom.

Similarly





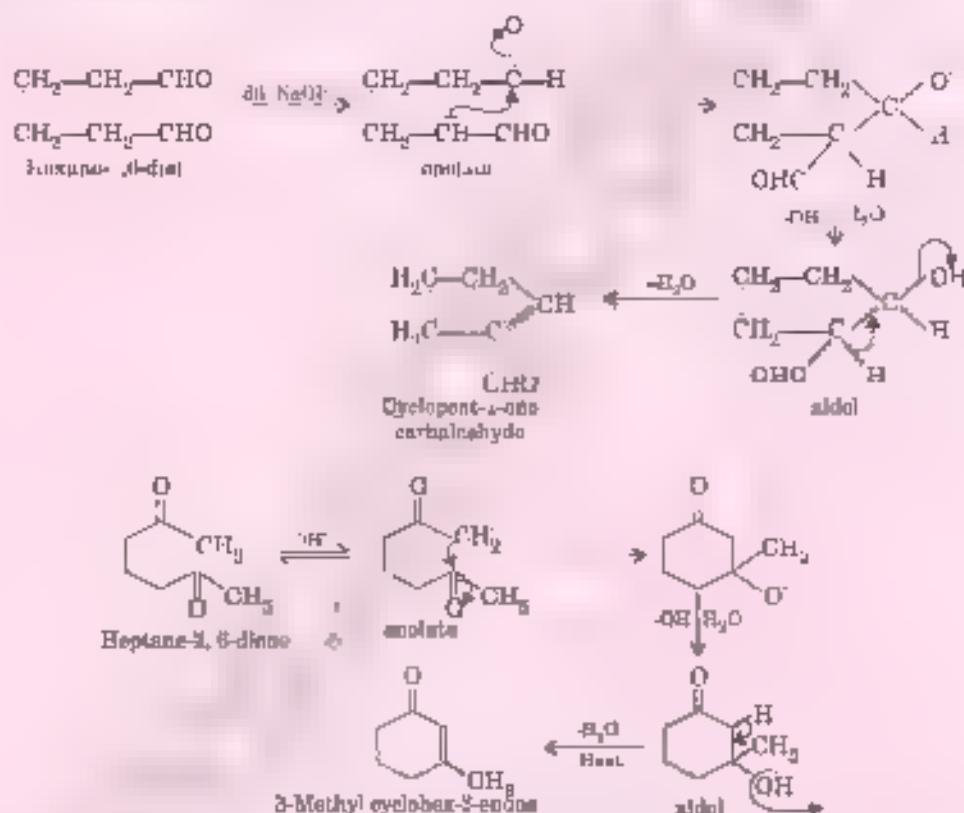
Divide the $\alpha-\beta-\gamma=\text{C}$ bond

For these, replace double bond to carbon with double bond to O and put back two H atoms on the α -carbon atom.

Learning Plan

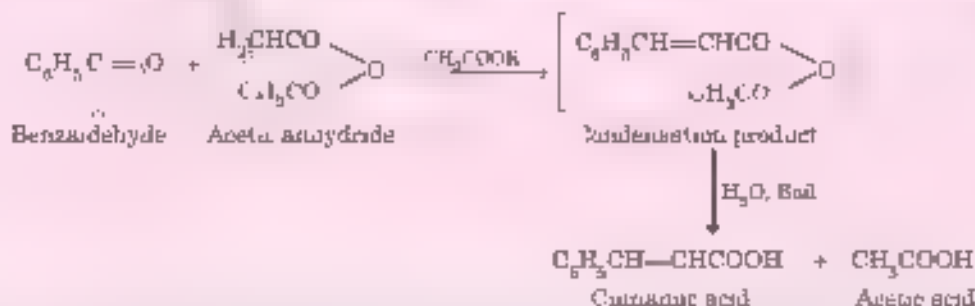
Intramolecular aldol condensation: Cyclisation via aldol condensation

If a compound contains two aldehyde/ketone groups or one aldehyde and one ketone group, then the enolate ion of one carbonyl group can add to the carbonyl group of the other. This reaction is called **intramolecular aldol condensation** and provides a convenient method to prepare five or six membered rings. This reaction is also called **aldol cyclization**. For example,

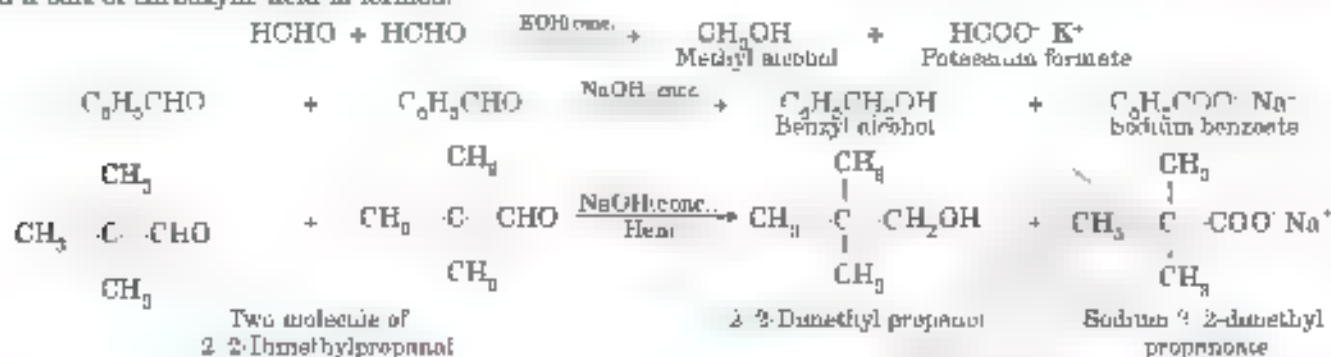


PERKIN CONDENSATION

It is an aldol type condensation in which aromatic aldehydes react with an aliphatic carboxylic acid anhydride to give an $\alpha-\beta$ -unsaturated acid. The catalyst commonly used is the sodium or potassium salt of the carboxylic acid. For example,



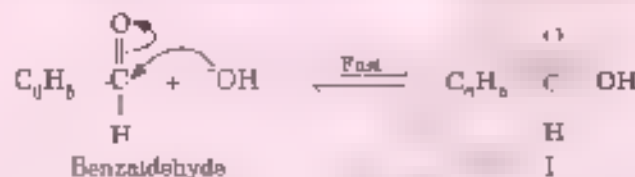
12. Cannizzaro's reaction. Aldehydes which do not contain any α -hydrogen atom such as formaldehyde (HCHO) and benzaldehyde ($\text{C}_6\text{H}_5\text{CHO}$) undergo self oxidation and reduction reaction on treatment with concentrated alkali. In this reaction, one molecule is oxidised to acid while another is reduced to alcohol. Thus, a mixture of an alcohol and a salt of carboxylic acid is formed.



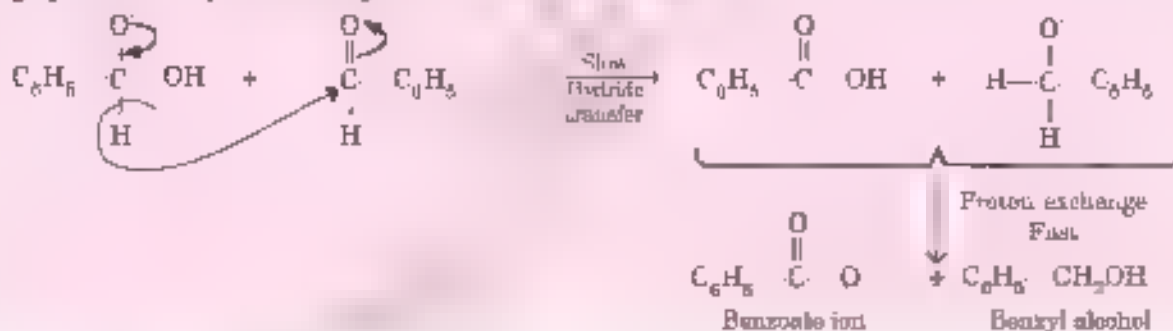
Mechanism : Mechanism of Cannizzaro's reaction

Cannizzaro's reaction is an example of hydride (H^-) transfer as shown below.

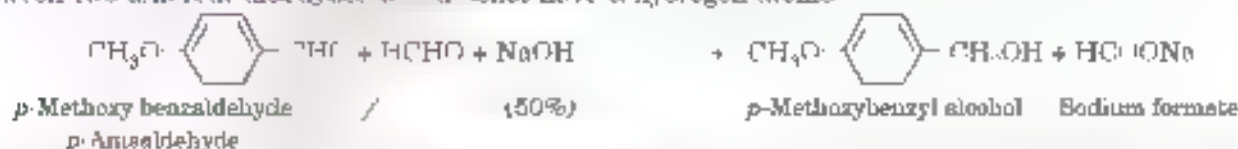
Step I The OH^- ion attacks the carbonyl carbon to form hydroxy alkoxide. It is a **nucleophilic attack** like other nucleophiles.



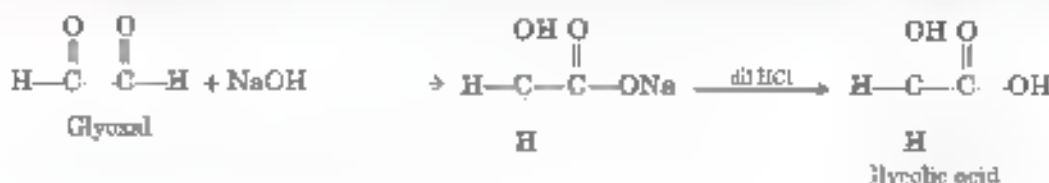
Step II The anion I acts as a hydride ion donor to the second molecule of aldehyde. The presence of negative charge on I helps in the loss of hydride ion. In the final step of the reaction the acid and the alkoxide ion exchange proton to acquire stability.



Cross Cannizzaro reaction. Like cross aldol condensation, cross Cannizzaro reaction can also take place between two different aldehydes which do not have α -hydrogen atoms.



Intramolecular or Cannizzaro reaction. We have so far considered the inter molecular Cannizzaro reaction in which the reaction takes place between two molecules of the same or different aldehydes. The intra molecular Cannizzaro reaction may also take place in which the same molecule undergoes oxidation as well as reduction. For example, glyoxal ($\text{CHO}-\text{CHO}$) does not have α -hydrogen atom but contains two aldehyde groups in the same molecule. It can undergo intra molecular Cannizzaro reaction in the presence of strong alkali to form glycolic acid.



13. Reaction with aluminium ethoxide (Tischenko reaction). This is a modified form of Cannizzaro reaction. All aldehydes with or without α -hydrogen can be made to undergo Cannizzaro reaction on treatment with aluminium ethoxide. However, under these conditions, the alcohol and the acid produced combine together to form ester. For example

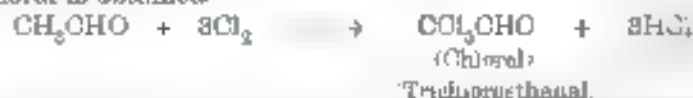


Similarly,



This reaction is called **Tischenko reaction**.

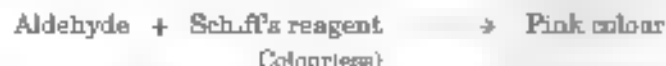
14. Halogenation. Aldehydes and ketones having α -hydrogen undergo halogenation under suitable conditions in which the hydrogens are successively replaced by halogen atoms. For example, when Cl_2 is bubbled through acetaldehyde, chloral is obtained.



Similarly, when Cl_2 is bubbled through warm acetone, a mixture of chloroacetones is obtained.



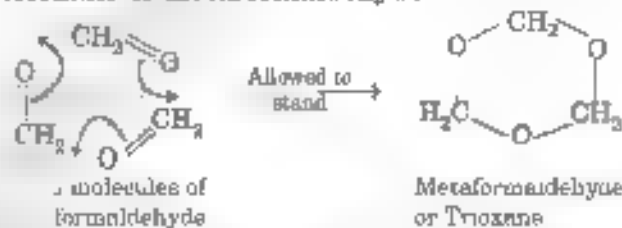
15. Action with Schiff's reagent. The Schiff's reagent is a pink coloured aqueous solution of rosaniline hydrochloride which has been decolourised by passing it through a solution of sodium bisulphite. When aldehydes are treated with bleached solution of Schiff's reagent, the pink colour is restored. This reaction is known as Schiff's test and is used as a test for aldehydes because ketones do not give this test.



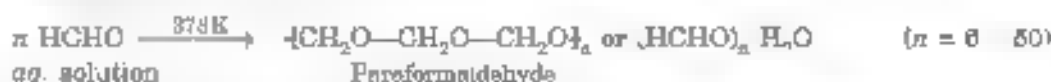
16. Polymerisation reactions. Aldehydes and ketones readily undergo polymerisation giving a variety of products.

(a) Polymerisation of methanal or formaldehyde. Formaldehyde undergoes polymerisation to form important polymers as discussed below.

When formaldehyde is allowed to stand at room temperature, it slowly undergoes polymerisation and forms a white solid called trioxane or metaformaldehyde.



When an aqueous solution (40%) of formaldehyde (formalin) is evaporated to dryness on a water bath, it forms a white solid called paraformaldehyde.

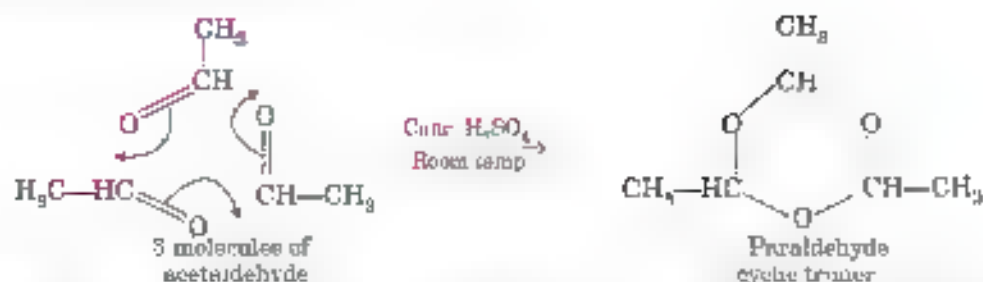


On heating, paraformaldehyde regenerates formaldehyde.

Formaldehyde condenses with phenol in the presence of a base such as NaOH and forms cross-linked polymer called **bakelite**. It is a synthetic plastic discussed in Unit 15.

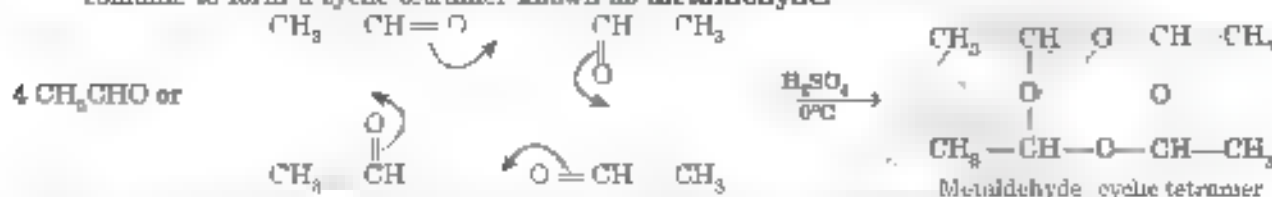
(b) Polymerisation of acetaldehyde. Some important polymers of acetaldehyde are:

When acetaldehyde is treated with a few drops of conc. H_2SO_4 at room temperature (298 K), rapid exothermic reaction occurs with the formation of a trimer called **paraldehyde**.



Paraldehyde is a sweet smelling liquid (b.p. 401 K) and is used in medicines as a **hypnotic**.

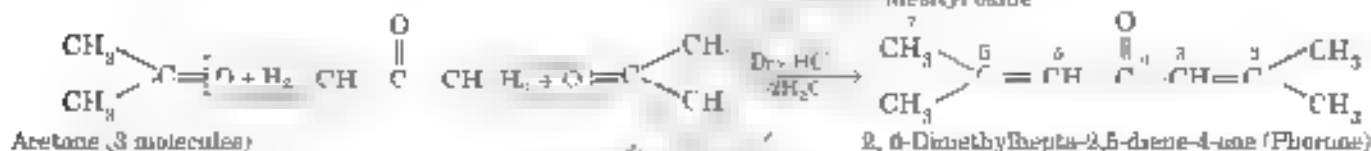
- (i) On cooling acetaldehyde with a few drops of conc. H_2SO_4 at 0°C or dry HCl gas at 0°C , four molecules combine to form a cyclic tetramer known as **metaldehyde**.



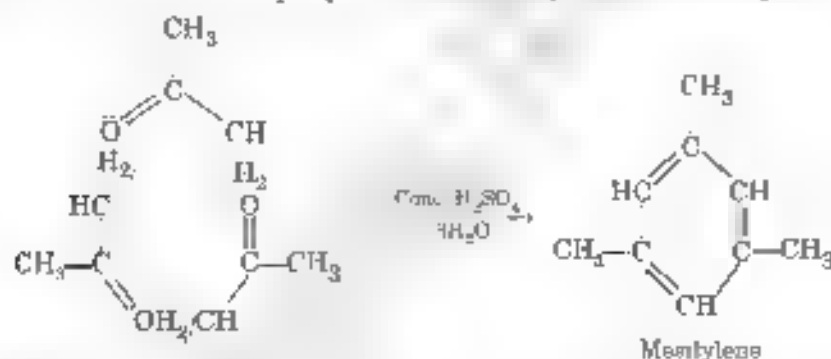
It is a white solid (b.p. 510 K) and regenerates acetaldehyde when distilled with dil. H_2SO_4 .

(ii) **Polymerisation of acetone.** Some important condensation products of acetone are

When treated with dry HCl gas it gives **mesityl oxide** and **phorone**.

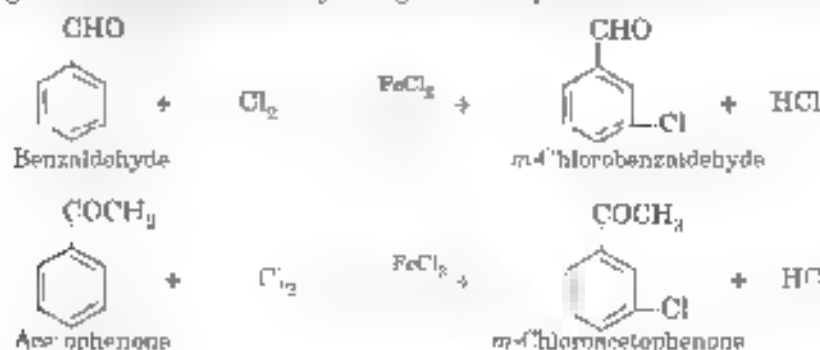


- (i) When treated with H_2SO_4 , three molecules get condensed to give mesitylene.

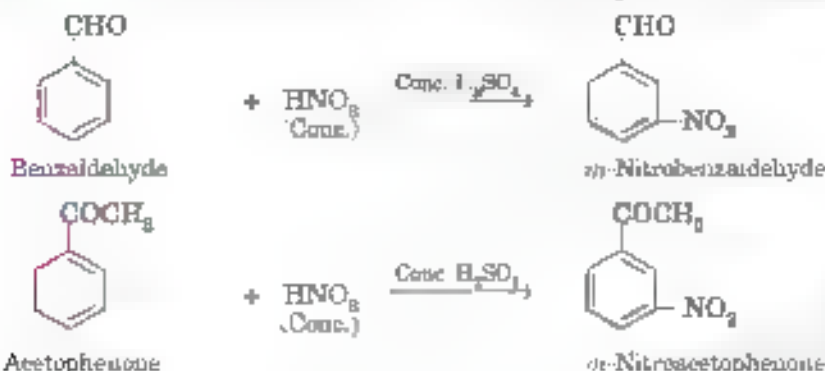


17. Substitution reactions of benzene nucleus in aldehydes and ketones. Aldehyde and ketone groups are **meta directing** groups and therefore, substitution reactions occur at meta positions. For example,

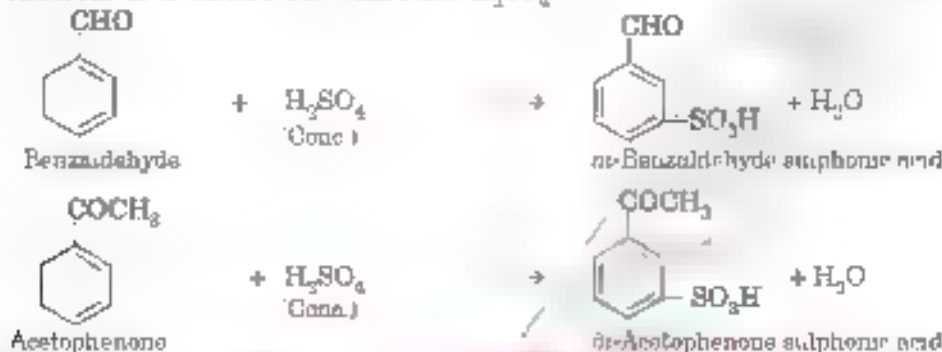
Halogenation. It is carried by halogen in the presence of ferric salt.



(i) **Nitration** is carried by nitrating mixture of conc. HNO_3 and conc. H_2SO_4 .



(ii) **Sulphonation.** It is carried out with conc. H_2SO_4 .



CONVERSIONS

Example 8

How will you bring about the following conversions in not more than two steps?

(a) Propanone to propene (D.S.B. 2017)

(b) Propanal to butanone

(c) Benzaldehyde to benzophenone

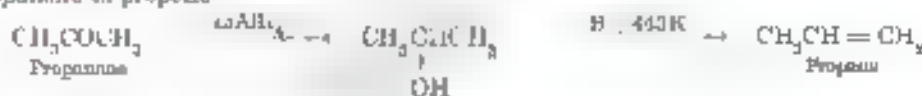
(d) Benzaldehyde to 3-phenylpropan-1-ol

(e) Benzaldehyde to α -hydroxyphenyl acetic acid

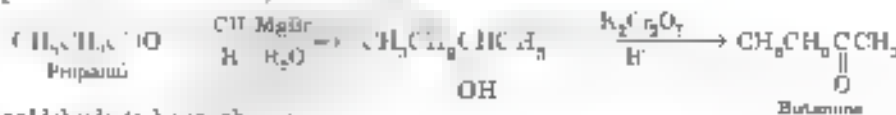
(f) Ethanal to 3-hydroxybutanal

Solution

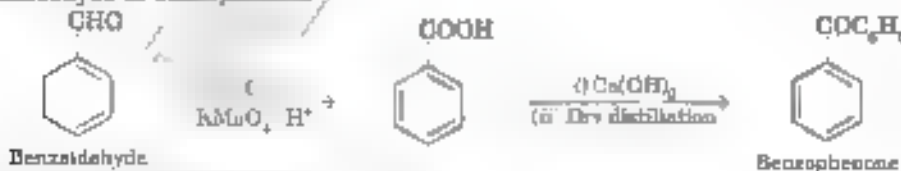
(a) Propanone to propene



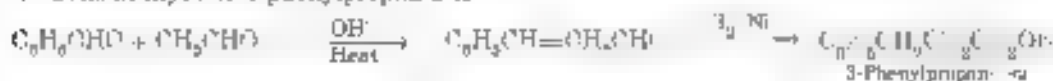
(b) Propanal to butanone



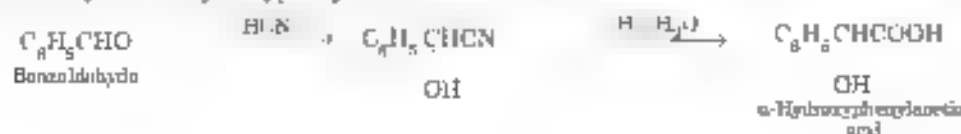
(c) Benzaldehyde to benzophenone



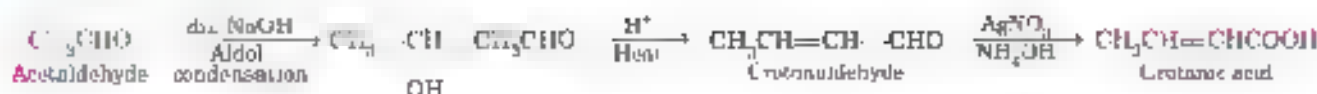
(d) Benzaldehyde to 3-phenylpropan-1-ol



(e) Benzaldehyde to α -hydroxyphenyl acetic acid



(f) Acetaldehyde to crotonic acid



□ Example 10.

An organic compound A with molecular formula $\text{C}_9\text{H}_8\text{O}$ forms an orange red precipitate with 2, 4-DNP reagent and gives yellow precipitate on heating with iodine in the presence of sodium hydroxide. It neither reduces Tollen's reagent or Fehling solution nor does it decolourise bromine water or Bayer's reagent. On drastic oxidation with chromic acid it gives a carboxylic acid B having molecular formula $\text{C}_7\text{H}_6\text{O}_2$. Identify the compound A and B and explain the reactions involved. [N.C.E.R.T. BSE Sample Paper 2007]

Solution :

(i) The compound A forms 2, 4-DNP derivative so, it is an aldehyde or ketone.

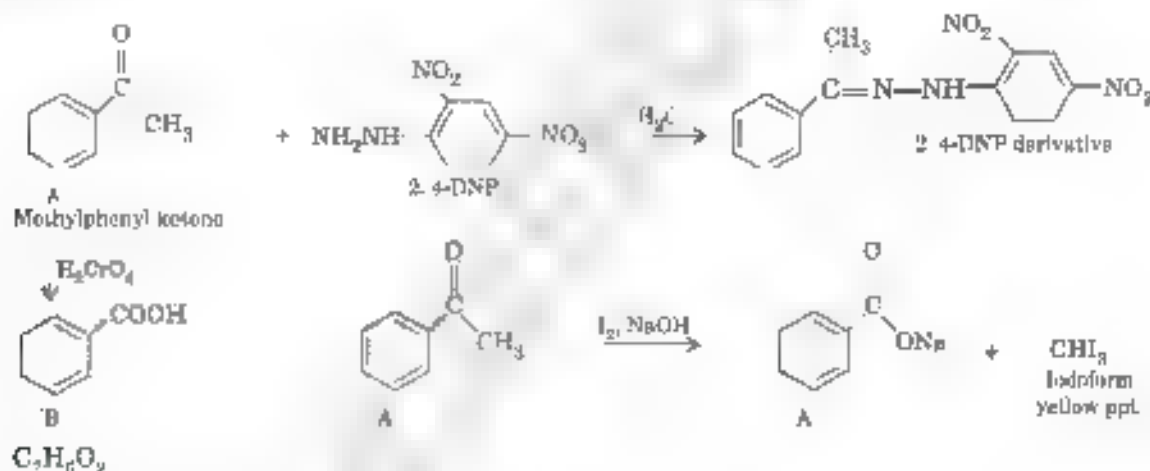
(ii) The compound does not reduce Tollen's reagent or Fehling solution so it must be a ketone.

(iii) The compound gives iodoform test so it should be a methyl ketone.

(iv) The molecular formula of A, $\text{C}_9\text{H}_8\text{O}$ indicates high degree of unsaturation, yet it does not decolourise Br_2 water or Bayer's reagent. This shows the presence of unsaturation due to the aromatic ring.

(v) The drastic oxidation with chromic acid, gives carboxylic acid B with molecular formula $\text{C}_7\text{H}_6\text{O}_2$ and it should be benzoic acid. Therefore the compound A should be monosubstituted aromatic methyl ketone. The molecular formula of A, indicates that it should be methyl phenyl ketone.

The reactions are



□ Example 11.

An unknown aldehyde A on reacting with alkali gives a β -hydroxy-aldehyde which loses water to form an unsaturated aldehyde, 2-butenal. Another aldehyde B undergoes disproportionation reaction in the presence of conc. alkali to form products C and D. C is an aryl alcohol with the formula $\text{C}_7\text{H}_7\text{O}$.

(i) Identify A and B

(ii) Write the sequence of reactions involved

(iii) Name the product when B reacts with zinc amalgam and hydrochloric acid. [CBSE Sample Paper 2007]

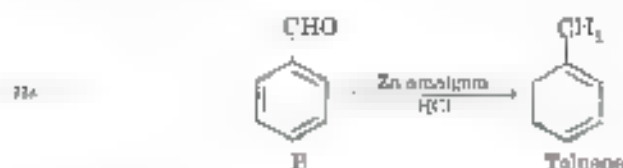
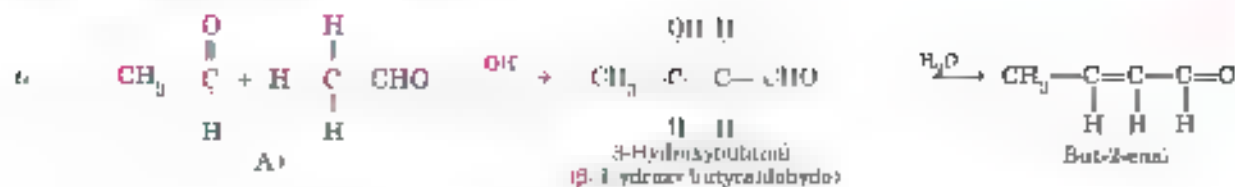
Solution :

The aldehyde compound A on reacting with alkali gives a β -hydroxy aldehyde which loses water to form unsaturated aldehyde but-2-enal. This is aldol condensation reaction.

The aldehyde compound B undergoes disproportionation reaction with conc. alkali. This is Cannizzaro's reaction.

The product C is an aryl alcohol with formula $\text{C}_7\text{H}_7\text{O}$. It must be $\text{C}_6\text{H}_5\text{CH}_2\text{OH}$ and is formed by condensation of benzaldehyde. Thus,



**Example 12**

A compound 'X' ($\text{C}_3\text{H}_4\text{O}$) on oxidation gives 'Y' ($\text{C}_3\text{H}_4\text{O}_2$). 'X' undergoes haloform reaction. On treatment with HCN, 'X' forms a product 'Z' which on hydrolysis gives 2-hydroxy propanoic acid.

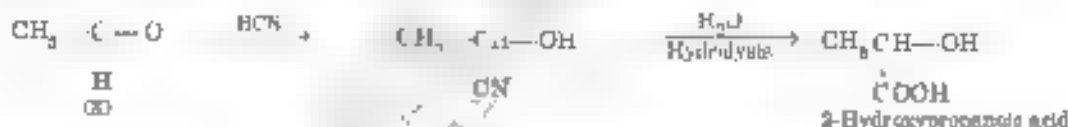
- (i) Write down structures of 'X' and 'Y'.
 (ii) Name the product when 'X' reacts with dil NaOH.
 (iii) Write down the equations for the reactions involved.

CBSE Sample Paper 2007 Assam & B. 2017

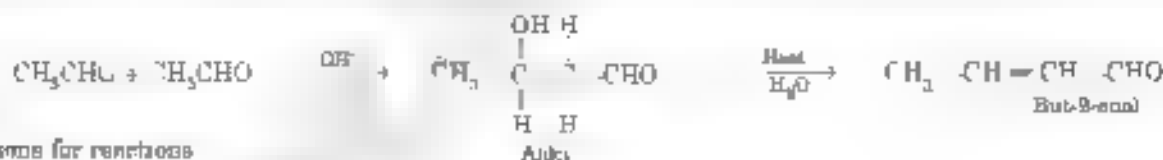
Solution

Compound 'X' ($\text{C}_3\text{H}_4\text{O}$) is oxidised to 'Y' ($\text{C}_3\text{H}_4\text{O}_2$). Since it undergoes haloform reaction, it must be acetaldehyde.
 $\therefore \text{X} = \text{CH}_3\text{CHO}$ Y = OH-CHO-CHO

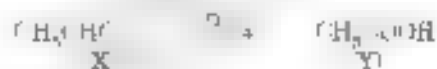
On treatment with HCN, 'X' gives cyanohydrin which on hydrolysis gives 2-hydroxypropanoic acid.



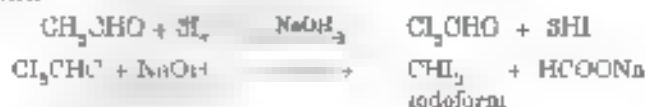
- (iv) When 'X' reacts with dil NaOH, it undergoes aldol condensation reaction forming aldol which on heating gives but-2-enal.



- (v) Equations for reactions



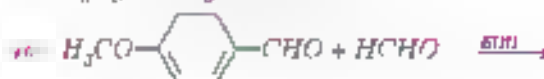
Haloform reaction



Other equations are given above

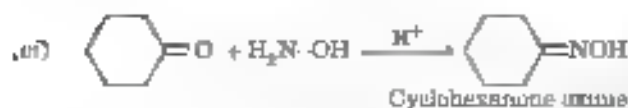
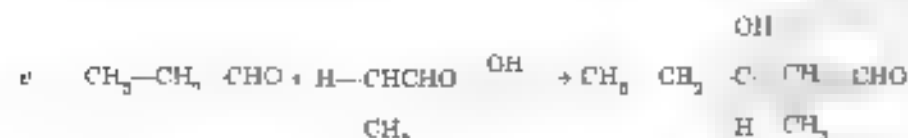
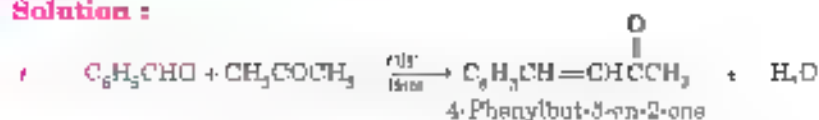
Example 13

Complete the following reactions



A.I.S.B. 2019

Solution :



□ Example 14.

Identify A, B, C, and D in the following reactions



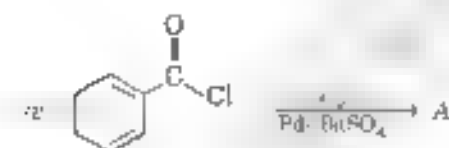
(Meghalaya S.B. 2019)



(Meghalaya S.B. 2019)



(Assam S.B. 2013, H.P.S.B. 2016)



(Assam S.B. 2015)



(Assam S.B. 2015, CBSE Sample Paper 2017-18)

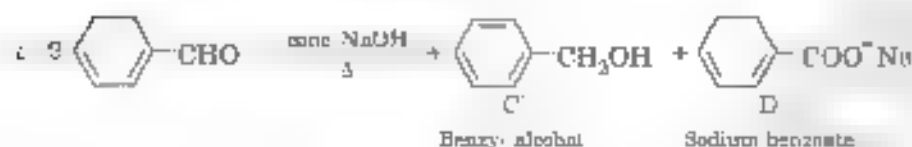
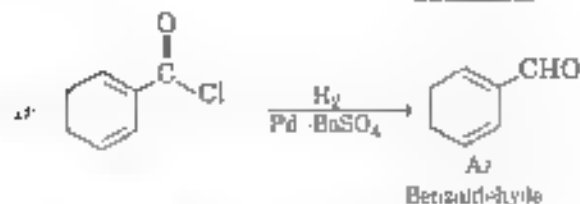
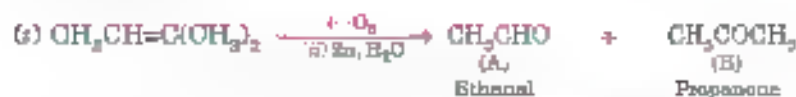


(Assam S.B. 2017, 2018)



(Meghalaya S.B. 2018)

Solution



□ **Example 16.**

16. An organic compound **A** has characteristic odor. On treatment with NaOH forms two compounds **B** and **C**. Compound **B** has molecular formula $\text{C}_7\text{H}_6\text{O}$ which on oxidation gives back **A**. The compound **C** is a sodium salt of an acid. When **C** is treated with soda lime it yields an aromatic hydrocarbon **D**. Deduce the structures of **A**, **B**, **C**, and **D**. Write the sequence of reactions involved.

6. Complete each synthesis by filling the missing starting materials, reagents or products. A, Y and Z.



¹⁰ *Hint: recall you bring about the following conversions in not more than two steps?*

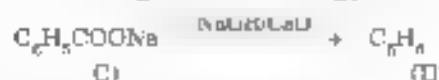
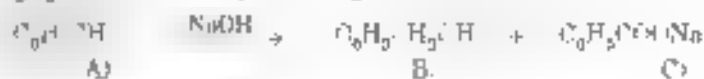
4. Toluene to benzaldehyde

(iii) *Ethylcyanide to 1-phenylpropanone.*

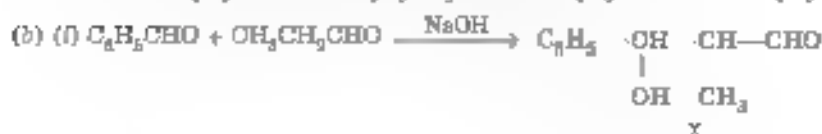
(CBSE Sample Paper 2011)

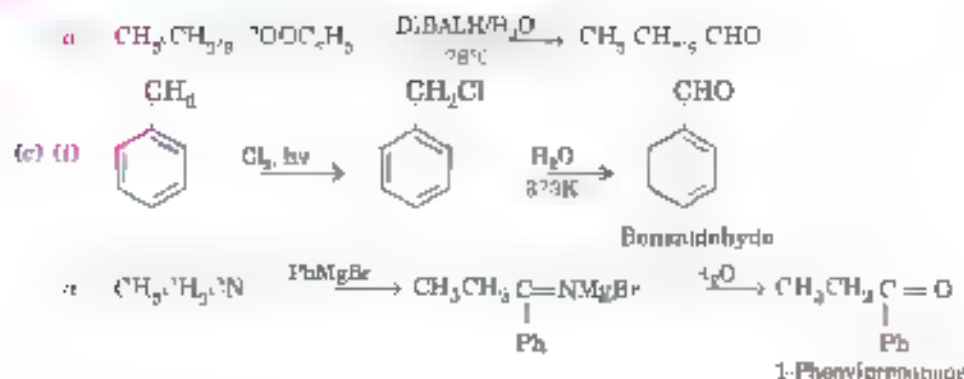
Solution 1

a. The compound A is C_6H_5CHO benzaldehyde having characteristic odour. The reactions are



A C_6H_5CHO ; B $-C_6H_5CH_2OH$; C $-C_6H_5COONa$; D $-C_6H_5$





Example 10.

(a) How do you convert the following?

- (i) Ethanal to propanone
(ii) Toluene to benzoic acid

OR

(b) A, B and C are three non-cyclic functional isomers of a carbonyl compound with molecular formula $\text{C}_4\text{H}_8\text{O}$. Isomers A and C give positive Tollens' test whereas isomer B does not give Tollens' test but gives positive iodoform test. Isomers A and B on reduction with Zn/Hg conc. HCl give the same product D.

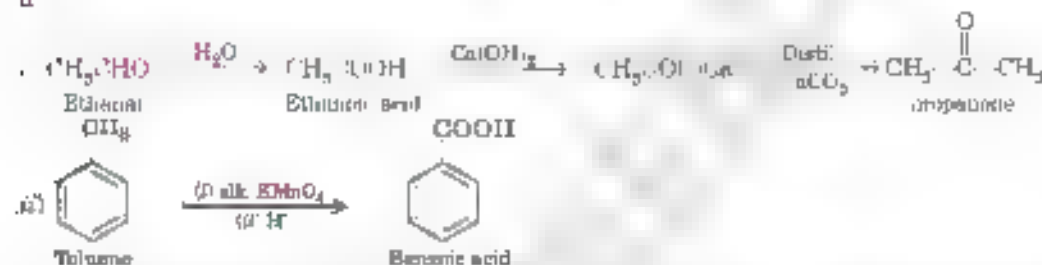
(c) Write the structures of (A), (B), (C) and (D).

Out of A, B and C isomers, which one is most reactive towards addition of HCN ?

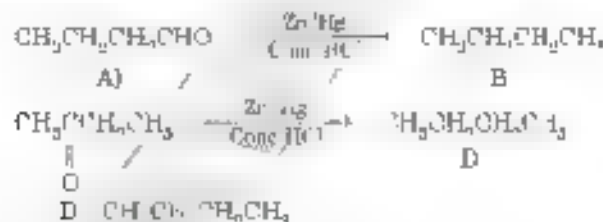
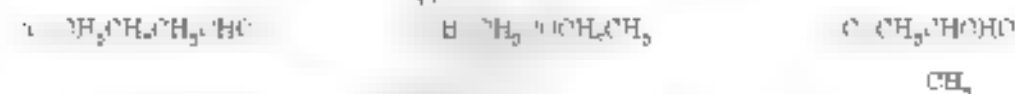
A.I.S.B. 2018

Solution :

a



(b) Out of A, B and C (A and C give positive Tollens' test and therefore, these are aldehydes. B does not give Tollens' test and therefore it is ketone. With $\text{C}-\text{CH}_3$ group because it gives positive iodoform test. Thus the three isomers are:



(c) $\text{CH}_3\text{COCH}_2\text{CH}_3$, B is least reactive

Example 17.

(a) An organic compound A has molecular formula $\text{C}_5\text{H}_{10}\text{O}$. It does not reduce Tollen's reagent but forms an orange precipitate with 2,4-DNP reagent. It does not give violet precipitate on treatment with NaOH and I_2 . Under vigorous conditions on oxidation it gives ethanoic acid and a carboxylic acid B. Sodium salt of B gives a hydrocarbon C in Kolbe's electrolytic reduction. Identify A, B and C and write the reactions involved.

(b) Predict the products formed in the following cases

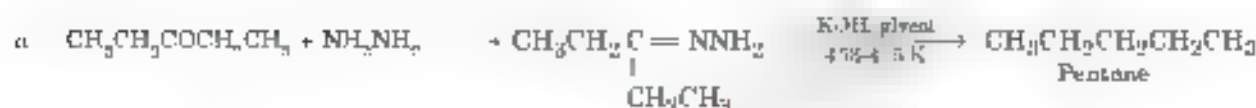
- (i) (A) reacts with PhMgBr and is then hydrolysed.
(ii) A reacts with hydrazine and is then heated with KOH and ethylene glycol.

(CBSE Sample Paper 2014)

Solution

a The compound A does not reduce Tollen's reagent but forms an orange precipitate with 2,4-DNP reagent, so it must be

ketone. Since it does not give iodoform test, it is not a methyl ketone. Therefore A is $\text{CH}_3\text{CH}_2\text{C(=O)CH}_2\text{CH}_3$ ($\text{C}_5\text{H}_{10}\text{O}$).



Practice Problems

12. Arrange the following in order of increasing boiling points.

(i) Propanone (ii) Propanal (iii) Propan-1-ol (iv) Propane (v) Dimethyl ether

• **Ans.** (iv) < (v) < (ii) < (i) < (iii)

13. Which of the following compounds would undergo aldol condensation, which the Cannizzaro's reaction and which neither? Write the structures of the expected products of aldol condensation and Cannizzaro's reaction.

(a) Benzaldehyde (b) Benzophenone (c) Cyclohexanone (d) Methanal
(e) 2-Methyl pentanal (f) Butan-1-ol (g) Phenyl acetaldehyde (h) 1-Phenyl propanone
(i) Methylamine (j) 2,2-Dimethyl butanal

• **Ans.** Aldol condensation: (a), (f), (g) Cannizzaro's reaction: (e) neither: (b), (c), (d), (h), (i), (j)

14. Write the names and structures of the products formed by the following reactions

- Addition of HCN to acetone
- Reaction of semicarbazide with formaldehyde
- Addition of Grignard reagent to acetone
- Reaction of acetophenone with hydrazine in strong base
- Reaction of PCl_5 and propanone.

15. What is the order of reactivity of the following towards HCN?

(i) $\text{C}_6\text{H}_5\text{CHO}$ (ii) $\text{C}_6\text{H}_5\text{COOC}_2\text{H}_5$ (iii) CH_3CHO (iv) HCHO

• **Ans.** $\text{HCHO} > \text{CH}_3\text{CHO} > \text{C}_6\text{H}_5\text{CHO} > \text{C}_6\text{H}_5\text{COOC}_2\text{H}_5$

16. Predict the product of reaction of

- acetone with aniline
- RCHO with hydrazine in the presence of KOH
- formaldehyde with ammoniac
- butanone with LiAlH_4
- aldehyde with Tollen's reagent
- acetone with KMnO_4

• **Ans.** (i) $(\text{CH}_3)_2\text{C} = \text{NNHC}_6\text{H}_5$ (ii) RCH_2NH_2 (iii) $(\text{CH}_3)_2\text{N}_2$ Urotropine
(iv) $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$ (v) Carboxylic acid (vi) No reaction.

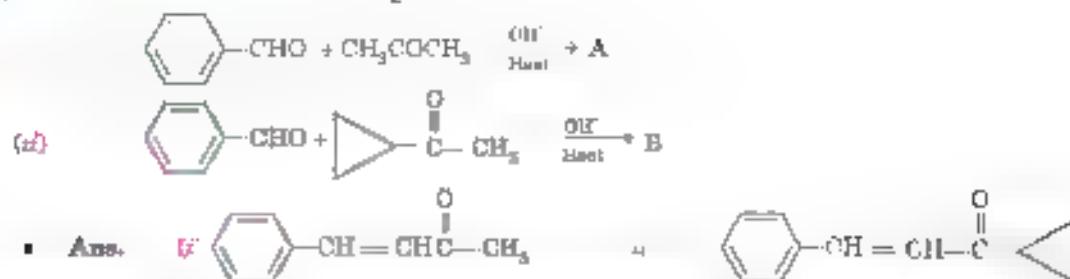


17. What Grignard reagent would use to make following conversions?

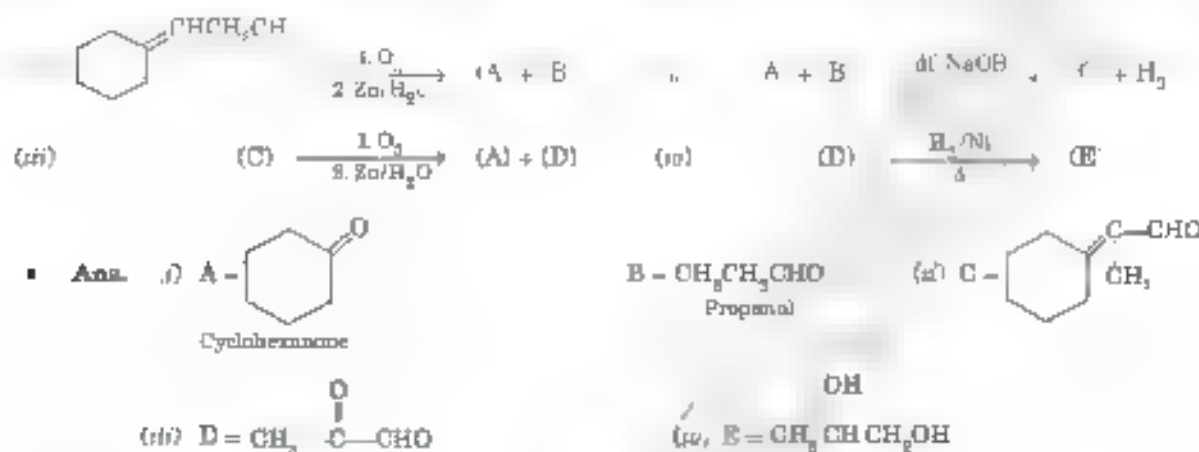
- Acetophenone to 2-phenyl-2-butanol
- Cyclohexanone to 1-propyl cyclohexanol
- Formaldehyde to benzyl alcohol

• **Ans.** (i) $\text{C}_3\text{H}_7\text{MgBr}$ (ii) $\text{CH}_3\text{CH}_2\text{CH}_2\text{MgBr}$ (iii) $\text{C}_6\text{H}_5\text{MgBr}$

18. What are A and B in the following reactions?



19. Identify the unknown organic compounds A to E in the following series of chemical reactions.



USES OF ALDEHYDES AND KETONES

Aldehydes and ketones are used in chemical industry as solvents, starting materials and reagents for the synthesis of other products. Some important uses of aldehydes and ketones are

(a) Uses of formaldehyde (methanal):

Formaldehyde is freely soluble in water. Its 40% solution in water is sold in market under the name **formalin**. Formaldehyde in the form of formalin (40% formaldehyde, 8% methanol and 52% water) is used for preserving biological specimens.

- It is also used in the manufacture of synthetic polymers like bakelite and synthetic dye stuffs like indigo.
- Formaldehyde is also used as an disinfectant.
- It is used in leather industry for tanning hides and as a reducing agent in silvering of mirrors and decolouring vat dyes.

(b) Uses of acetaldehyde (ethanal):

- Acetaldehyde is used in the commercial preparation of a number of organic compounds such as acetic acid, ethyl acetate, *n*-butyl alcohol, etc.
- Paraldehyde is used in medicines as a hypnotic.
- Acetaldehyde is also used in silvering of mirrors.

(c) Uses of benzaldehyde:

- It is used as an important flavouring agent in perfume industry.
- It is also used as a starting material for the synthesis of many other organic compounds such as mandelic acid, benzoyl chloride, etc.
- It is used in the manufacture of dyes like malachite green.

(d) Uses of acetone (propanone):

- It is very important solvent and is extensively used as a solvent in industries and laboratories.
- It is used in the preparation of chloroform, diacetone alcohol.
- It is used in the manufacture of thermosetting plastic **Permapex**.
- It is used as one of the constituents of liquid nail polish.

Many aldehydes and ketones such as butyraldehyde, vanillin, acetophenone, camphor etc are known for their odours and flavours.

DISTINCTION BETWEEN ALDEHYDES AND KETONES

Aldehydes and ketones can be distinguished by the following tests

Test	Aldehydes	Ketones
1. With Tollen's reagent	Form silver mirror	No silver mirror
2. With Fehling solution	Give red precipitate	No precipitate
3. With Schiff's reagent	Give pink colour	No colour
4. Reduction with LiAlH_4	Primary alcohols are formed	Secondary alcohols are formed
5. Action with alcohol in the presence of HCl	Form acetals easily	Do not form acetals easily

DISTINCTION BETWEEN SOME PAIRS OF CHEMICAL TESTS

1. Formaldehyde and acetaldehyde

Acetaldehyde gives yellow ppt. of iodoform with an a.k.n. reaction of iodine

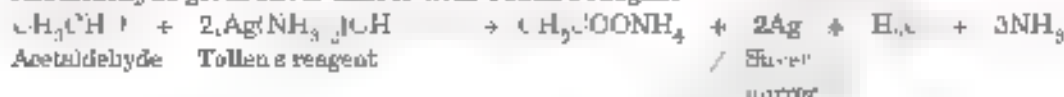


Acetaldehyde

Formaldehyde does not give this test.

2. Acetaldehyde and acetone

i) Acetaldehyde gives silver mirror with Tollen's reagent.



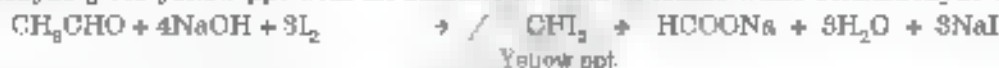
Acetone does not give this test

ii) Acetaldehyde gives red ppt. with Fehling solution.



2. Benzaldehyde and acetaldehyde

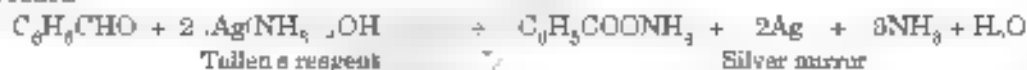
Acetaldehyde gives yellow ppt with an alkaline solution of Iodine while benzaldehyde does not give ppt



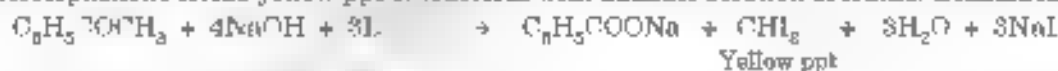
Benzaldehyde does not give ppt.

4. Benzaldehyde and acetophenone

• Benzaldehyde forms silver mirror with ammoniacal silver nitrate solution (Tollen's reagent). Acetophenone does not react.



* Acetophenone forms yellow ppt of iodoform with alkaline solution of iodine. Benzaldehyde does not react.



6. Pentan-3-one and pentan-2-one

• Pentan-2-one forms yellow ppt with alkaline solution of iodine. Pentan-3-one does not give yellow ppt.



1. Pentan-2-one gives white ppt with sodium bisulphite while pentan-3-one does not give.



6. Acetophenone and benzophenone

Acetophenone gives yellow ppt with alkaline solution of iodine. Benzophenone does not give this test.



add on

Conceptual Questions 1

Q. 1. Why do aldehydes and ketones have high dipole moments?

Ans. The carbonyl group in aldehydes and ketones contains a double bond between carbon and oxygen atoms. Since oxygen is more electronegative than carbon, the carbonyl group is a polarised group.



Oxygen gets a considerable negative charge while carbon gets a considerable positive charge. Therefore, aldehydes and ketones have high dipole moments.

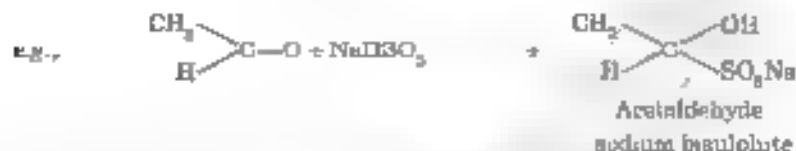
Q. 2. How does $>C=C<$ differ from $>C=O$ group in chemical reactions?

Ans. The ethylenic double bond differs from carbonyl group in the following ways:

- i. Halogens, halogen acids and H_2SO_4 undergo addition reactions with ethylenic double bond but not with carbonyl group.
- ii. Ethylenic double bond undergoes electrophilic addition reactions while $>C=O$ bond undergoes nucleophilic addition reactions.

Q. 3. Sodium bisulphite is used for the purification of aldehydes and ketones. Explain.

Ans. Aldehydes and ketones react with sodium bisulphite to form addition compounds.



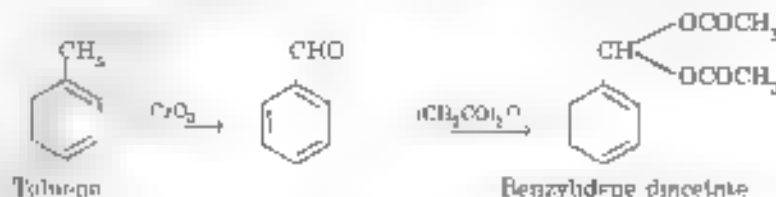
The addition products are crystalline solids. These can be decomposed by mineral acids or aqueous alkalis to give back the original aldehyde or ketone. Therefore this reaction can be used for the purification of aldehydes and ketones.

Q. 4. In the preparation of acetaldehyde from ethyl alcohol, it is distilled out as soon as it is formed. Explain.

Ans. Aldehyde is easily oxidisable to acetic acid. Therefore to prevent its oxidation, it is distilled out as soon as it is formed.

Q. 5. Oxidation of toluene with CrO_3 to benzaldehyde is carried out in the presence of acetic anhydride.

Ans. During the oxidation of toluene with CrO_3 , as soon as benzaldehyde is formed, it reacts with acetic anhydride to form benzylidene diacetate. This checks the further oxidation of benzaldehyde to benzoic acid.



Q. 6. Aliphatic aldehydes do not show position isomers. Why?

Ans. In case of aliphatic aldehydes, the $-CHO$ group is always present at the end. Therefore, they do not show position isomerism.

Q. 7. Aldehydes and ketones have lower boiling points than corresponding alcohols and acids. Explain. [A.I. S.B. 2019]

Ans. Aldehydes and ketones are polar compounds having sufficient intermolecular dipole-dipole interactions between opposite ends of $>C=O$ dipoles. However, these dipole-dipole interactions are weaker than the intermolecular hydrogen bonds present in alcohols and carboxylic acids. Therefore, boiling points of aldehydes and ketones are lower than alcohols and carboxylic acids.

Q. 8. Distinguish between



[A.I. S.B. 2016]

Ans. Heat both the compounds with $NaOH$ and I_2 . $C_6H_5CH=CH-COCH_3$ gives yellow ppt. of iodoform. $C_6H_5CH=CH-COCH_2CH_3$ does not give yellow ppt. of iodoform.

Q.9. What is formalin ?

(H.P. S.B. 2010)

Ans. Formalin is a 40% aqueous solution of formaldehyde

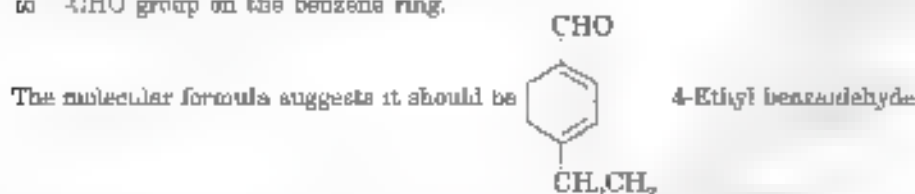
Q.10. Give the different products obtained when but-1-yne undergoes

- Hydroboration oxidation reaction
- Hydration in the presence of Hg^{2+} and H^+



Q.11. An organic compound with molecular formula $\text{C}_8\text{H}_8\text{O}$ forms 2, 4-DNP derivative, reduces Tollen's reagent and undergoes Cannizzaro reaction. On vigorous oxidation it gives 1, 4-benzenedicarboxylic acid. Identify the compound. (Meghalaya S.B. 2015)

Ans. The given compound forms 2, 4-DNP derivative. Therefore, it is an aldehyde or ketone. Since it reduces Tollen's reagent it must be aldehyde. The compound undergoes Cannizzaro's reaction, so it does not contain α -hydrogen. On vigorous oxidation it gives 1, 4-benzenedicarboxylic acid, it means that it must be containing alkyl group at 4-position with respect to $-\text{CHO}$ group on the benzene ring.



Q.12. Arrange the following in the increasing order of their reactivity in nucleophilic addition reactions.



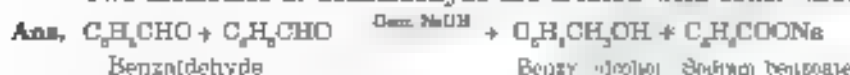
(A.I.S.B. 2016)

Ans. $\text{C}_6\text{H}_5\text{CHO} < \text{CH}_3\text{CHO} < \text{HCHO}$

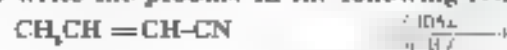
Q.13. Explain with the help chemical reaction:

Two molecules of benzaldehyde are treated with conc. NaOH .

(Meghalaya S.B. 2016)



Q.14. Write the product in the following reaction:



(A.I.S.B. 2017)

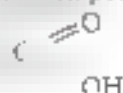


PART B

CARBOXYLIC ACIDS

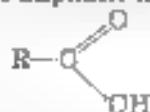
CARBOXYLIC ACIDS

Carboxylic acids are the compounds containing the carboxyl functional group



in their molecules. The carboxyl group is made up of carbonyl, $\text{C}=\text{O}$ and hydroxyl, $-\text{OH}$ groups and therefore, the name carboxyl is derived from *carbo* (from carbon) and *oxy* (from hydroxyl) group.

The carboxylic acids may be *aliphatic* $\text{R}-\text{COOH}$ or *aromatic* $\text{Ar}-\text{COOH}$ depending upon whether $-\text{COOH}$ group is attached to aliphatic alkyl chain or aryl group respectively. The general formula is



Aliphatic carboxylic acid
(where R = H or any alkyl group)



Aromatic carboxylic acid
(where Ar is any aryl group)

Some higher members of aliphatic carboxylic acids C_{10} – C_{25} are known as **fatty acids** because some of these are obtained by the hydrolysis of fats. They occur in natural fats as esters of glycerol. Carboxylic acids serve as starting materials for many other important organic compounds such as anhydrides, esters, acid chlorides, amides, etc.

NOVENCLATURE OF CARBOXYLIC ACIDS

Aliphatic and aromatic carboxylic acids are classified as *mono*-, *di*-, *tri*- or *poly*-carboxylic acids according as they contain *one*, *two*, *three* or *many* carboxylic acids in their molecules.

Monocarboxylic acids

The common or trivial names of carboxylic acids are based on their sources of origin. For example, formic acid $HCOOH$ is so named because it was first obtained from red ants (Latin *formica* means ants). Similarly, acetic acid CH_3COOH is so named because it was obtained from vinegar (Latin *acetum* meaning vinegar). Lactic acid $CH_3CH(OH)COOH$ from rancid butter (Latin *butyrum* meaning butter), caproic acid $CH_3(CH_2)_4COOH$ from goats (Latin *capra* meaning goat), etc.

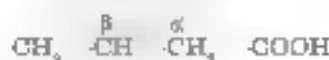
In common system, the position of the substituents is indicated by the Greek letters (α , β , γ , δ , etc.).

The carbon atom adjacent to the carboxyl carbon is assigned the letter α , the next carbon on chain as β and so on.

For example, $\begin{array}{c} \text{O} \\ \parallel \\ \text{C} \\ | \\ \text{C} - \text{O} - \text{H} \\ | \\ \text{H} \end{array}$



CH_3
 α -Methylpropionic acid
(isobutyric acid)



CH_3
 β -Methylbutyric acid
(isovaleric acid)

According to IUPAC system, the name of the acid is derived from the corresponding alkane by replacing the terminal 'e' with '-oic' and adding the word **acid**. The position of the substituents is indicated by the following rules:

1. The longest chain containing the carboxylic group $-\text{COOH}$ is selected.
2. The carbon chain is numbered from the carboxylic acid group. The carbon of carboxyl group is always given number 1.
3. The position of the substituents is indicated by the number. For example,



Methanoic acid



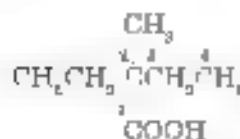
Ethanoic acid



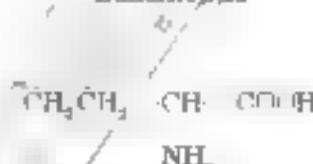
Br
2-Bromobutanoic acid



CH_3
2-Methylbutanoic acid



2-Ethyl-2-methylbutanoic acid



2-Aminobutanoic acid



3-Methyl-3-oxopropanoic acid



3-Oxobutanoic acid



2-Phenylethanoic acid



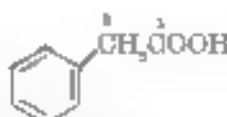
3-Phenylpropanoic acid



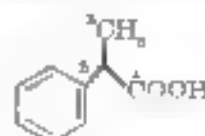
4-Chlorocyclohexan-1-carboxylic acid



Hexa-2,4-dienoic acid



2-Phenylethanoic acid
(Phenylacetic acid)



1-Phenylpropanoic acid

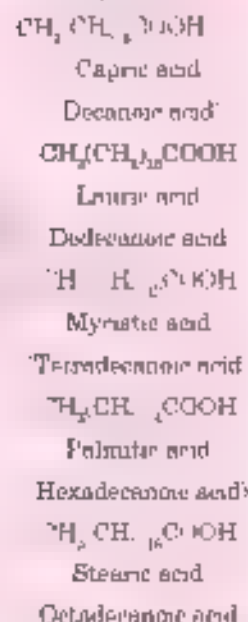


Formyl methanoic acid
or Oxoethanoic acid

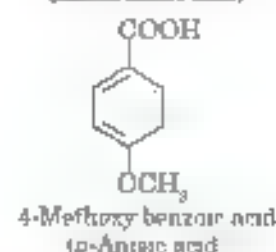
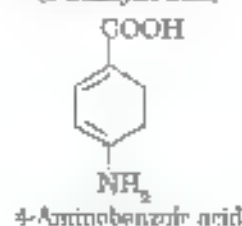
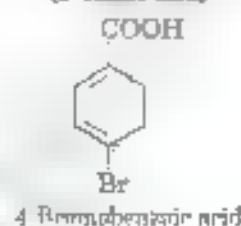
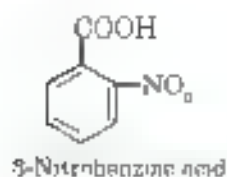
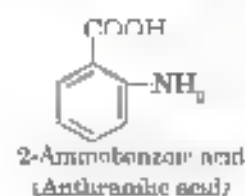
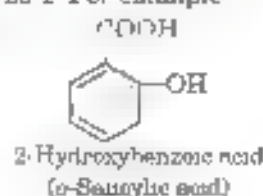
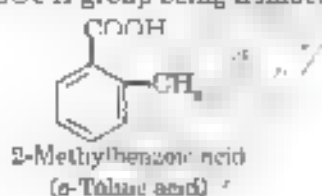
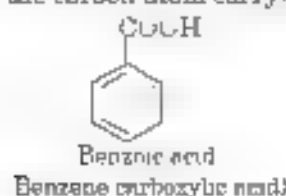
The common and IUPAC names of some monocarboxylic acids are given below

Monocarboxylic acid	Common name	IUPAC name
HCOOH CH_3COOH $\text{CH}_3\text{CH}_2\text{COOH}$ $\text{CH}_3\text{CH}_2\text{CH}_2\text{COOH}$ CH_3CHCOOH	Formic acid Acetic acid Propionic acid <i>n</i> -Butyric acid Isobutyric acid (α -Methylpropionic acid)	Methanoic acid Ethanoic acid Propanoic acid Butanoic acid 2-Methylpropanoic acid
$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{COOH}$ $\text{CH}_3\text{CH}_2\text{CH}_2\text{COOH}$ $\text{OHC}-\text{COOH}$ $\text{CH}_3-\text{CH}(\text{CH}_3)\text{COOH}$ $\text{CH}_3\text{CH}_2\text{CH}(\text{CH}_3)\text{COOH}$ $\text{CH}_2=\text{CHCOOH}$ $\text{CH}_3-\text{CH}=\text{CHCOOH}$ $\text{CH}_3\text{CH}=\text{CHCOOH}$ $\text{C}_6\text{H}_5\text{CH}=\text{CHCOOH}$ $\text{C}_6\text{H}_5\text{CH}_2\text{CH}(\text{OH})\text{COOH}$	Valeric acid <i>n</i> -Caproic acid Glyoxylic acid Isovaleric acid α -Hydroxy propionic acid or Lactic acid Acrylic acid Crotonic acid Cinnamic acid Mandelic acid	Pentanoic acid Hexanoic acid Oxoethanoic acid 3-Methylbutanoic acid 2-Hydroxypropanoic acid Prop-2-enoic acid But-2-enoic acid 3-Phenylprop-2-enoic acid 2-Hydroxy-2-phenylpropanoic acid

Some higher popular carboxylic acids



The simplest aromatic acid is **benzoic acid**. The IUPAC names of the substituted acids are derived by prefixing the name of the substituent to the name of parent acid i.e. benzoic acid and the position is indicated by an Arabic numeral, with the carbon atom carrying the $-\text{COOH}$ group being numbered as 1. For example

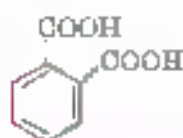


Dicarboxylic acids

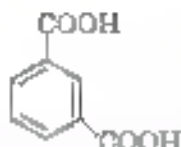
These contain two carboxylic acid groups, one at each end of a hydrocarbon chain. These are named as **alkanedioic acids**. Most dicarboxylic acids have common names

Dicarboxylic acid	Common name	IUPAC name
$\text{HOOC}-\text{COOH}$	Oxalic acid	Ethanedioic acid
$\text{CH}_2(\text{COOH})_2$	Malonic acid	Propanedioic acid
$\text{CH}_2\text{CH}_2(\text{COOH})_2$	Succinic acid	Butanedioic acid
$\text{HOOC}-\text{CH}_2-\text{CH}_2-\text{COOH}$ $\text{HOOC}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{COOH}$	Glutaric acid Adipic acid	Pentanedioic acid Hexanedioic acid
$\text{HOOC}-\overset{1}{\text{CH}_2}-\overset{2}{\text{CH}}(\text{COOH})-\overset{3}{\text{CH}_2}-\overset{4}{\text{COOH}}$	α -Acetyl-succinic acid	2-(1-Oxoethyl) butane-1,4-dioic acid

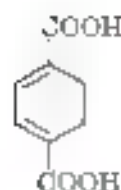
The common aromatic dicarboxylic acids are



Benzene-1,2-dicarboxylic acid
(Phthalic acid)



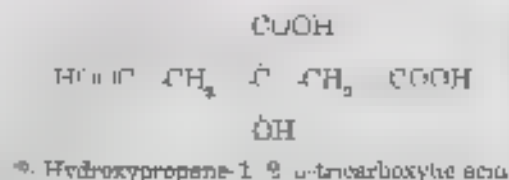
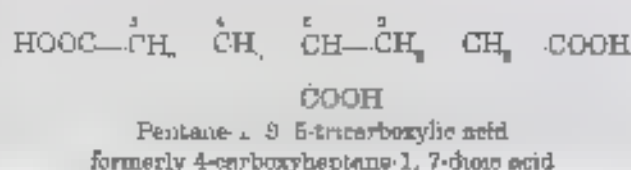
Benzene-1,3-dicarboxylic acid
(Isophthalic acid)



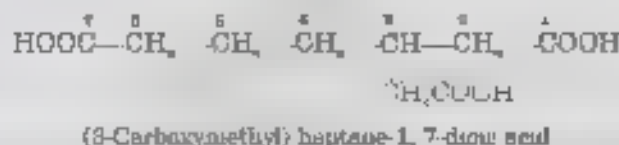
Benzene-1,4-dicarboxylic acid
(Terephthalic acid)

IUPAC Recommendations for Carboxylic Acids containing more than two COOH groups

According to latest IUPAC recommendations if an unbranched chain is directly bonded to more than two like functional groups, the organic compound is named as a derivative of parent alkane which does not include the carbon atoms of the functional groups. These are named by the use of suffix such as tri-carboxylic acid (for three COOH groups). For example,

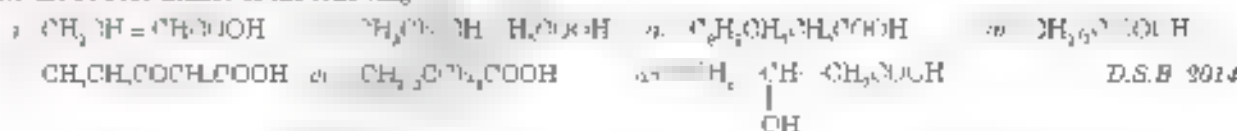


However, if three COOH groups are not directly linked to the unbranched chain, the two like groups are considered as the parent chain and are named by using the suffix *di* before the name of the functional group. The third group forming the side chain is considered as a **substituent group**. For example,



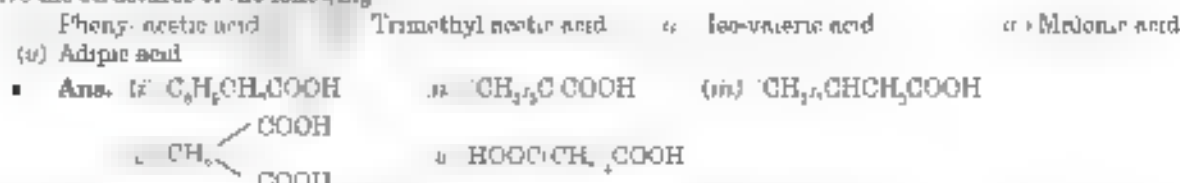
Practice Problems

20. Write the IUPAC names of the following



- Ans. (i) 3-Pentanonic acid (ii) Pentanoic acid (iii) 3-Phenylpropanoic acid
 (iv) 2,3-Dimethylpropanoic acid (v) 3-Oxopentanoic acid (vi) 3,3-Dimethylbutanoic acid
 (vii) 3-Hydroxybutanoic acid

21. Give the structures of the following



22. Write the IUPAC names of the following acids whose common names are given

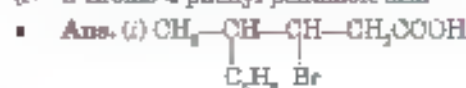
- (i) Isobutyric acid (ii) n-Valeric acid (iii) Succinic acid (iv) Phenylacetic acid
 (v) Malonic acid
- Ans. (i) 2-Methylpropanoic acid (ii) Pentanoic acid (iii) Butanedioic acid (iv) Phenylacetic acid
 (v) Propanedioic acid

23. Write the functional isomers of propanoic acid.

- Ans. Methyl ethanoate, $\text{CH}_3\text{COOCH}_3$

24. Draw the structures of the following

(a) 3-Bromo-4-phenyl pentanoic acid



(ii) Hex-5-en-4-ynoic acid



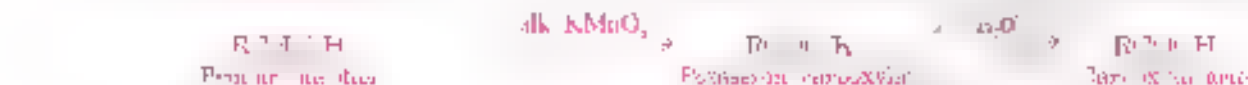
(A.I.S.B 90/95)

METHODS OF PREPARATION OF CARBOXYLIC ACIDS

Some of the general methods for the preparation of carboxylic acids are described below

1 From oxidation of primary alcohols Primary alcohols are readily oxidised to carboxylic acids with oxidising agents such as potassium permanganate (KMnO_4), potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$) in neutral, alkaline or acidic media and chromic anhydride (CrO_3) in acidic media. The oxidation with $\text{K}_2\text{Cr}_2\text{O}_7$ or CrO_3 in acidic media generally gives some amount of esters. Therefore oxidation with KMnO_4 in neutral or alkaline media is preferred for the preparation of carboxylic acids.

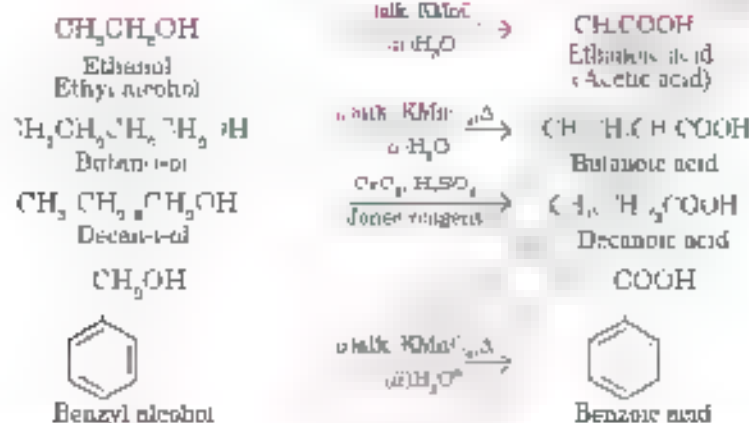
The acid is first obtained as its potassium salt, which on treatment with mineral acids gives carboxylic acid.



or simply as



e.g.,



NOTE

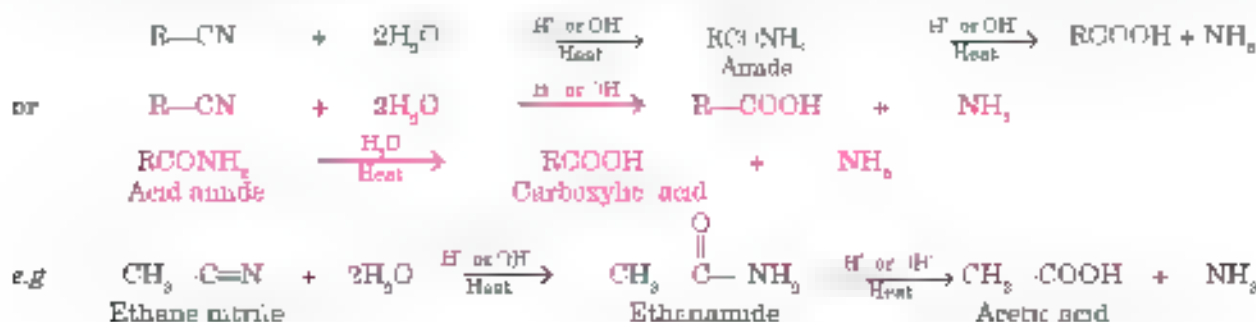
$\text{CrO}_3/\text{H}_2\text{SO}_4$ in aqueous solution is called Jones's reagent.

2 From oxidation of aldehydes and ketones. Aldehydes are easily oxidised to carboxylic acids even with mild oxidising agents like Tollen's reagent.

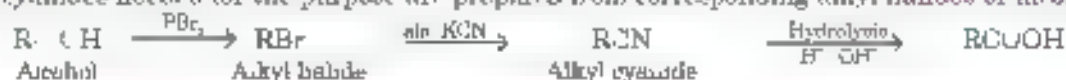


Ketones are oxidised with difficulty and usually a mixture of acids is obtained.

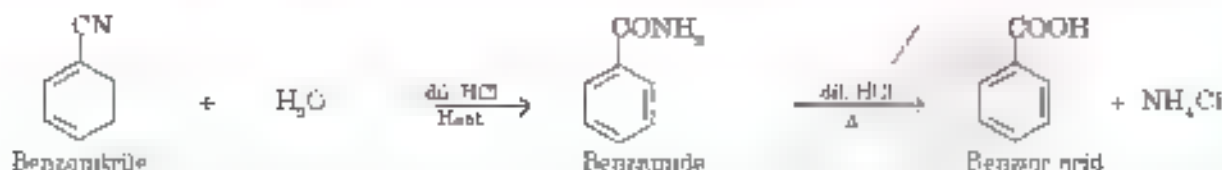
3 From hydrolysis of nitriles or cyanides and amides. The nitriles are hydrolysed in dilute aqueous acidic or alkaline medium. The alkyl nitriles are first hydrolysed to amides in the presence of acid or alkali and then to acids.



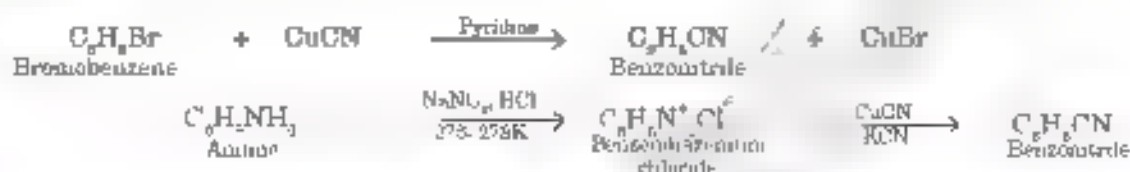
The alkyl cyanides needed for the purpose are prepared from corresponding alkyl halides or alcohols as



It may be noted that the acid produced contains one more carbon atom than the original alkyl halide or alcohol. Thus, the hydrolysis of nitriles provides a useful method for the preparation of carboxylic acids containing one more carbon atom than the starting alkyl halide or alcohol.

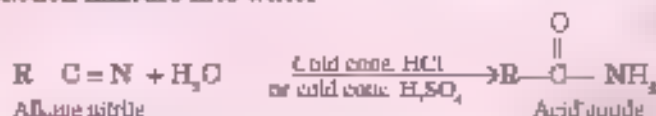


The aryl nitriles needed for the purpose are prepared either from the corresponding aryl halides or arylamines via diazonium salts as shown below

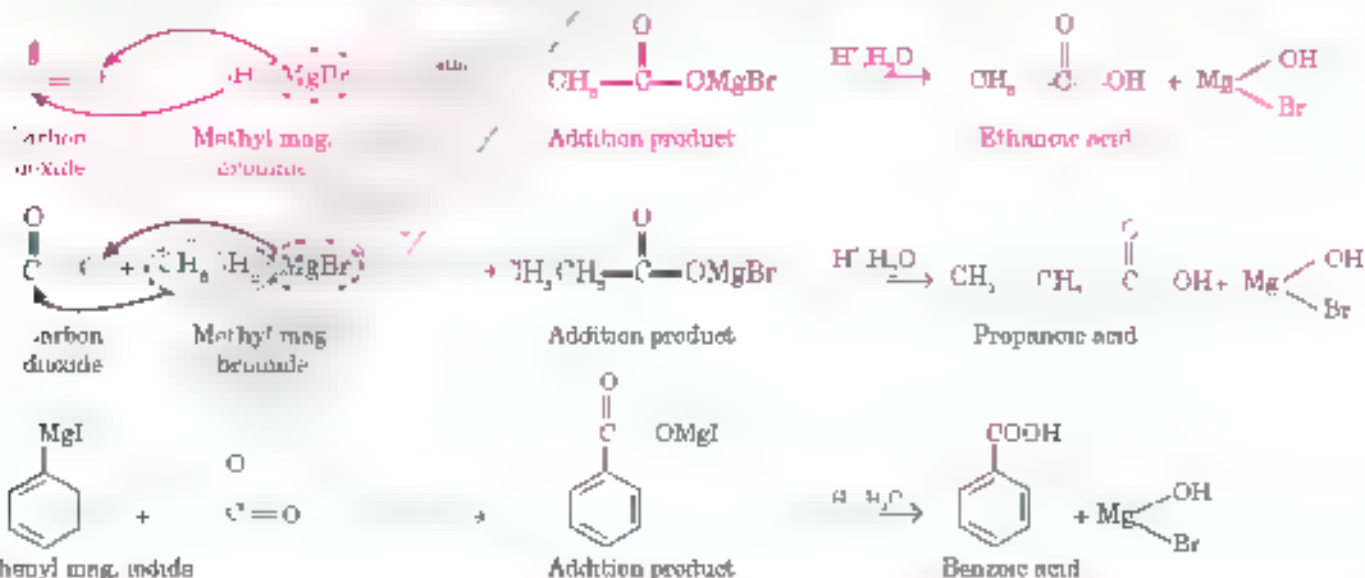


NOTE

It may be noted that mild conditions are used to stop the reaction at amide stage. For example, amides are produced by shaking the nitriles with cold conc. HCl or by dissolving the nitriles in cold conc. H₂SO₄ and then pouring the reaction mixture into water.

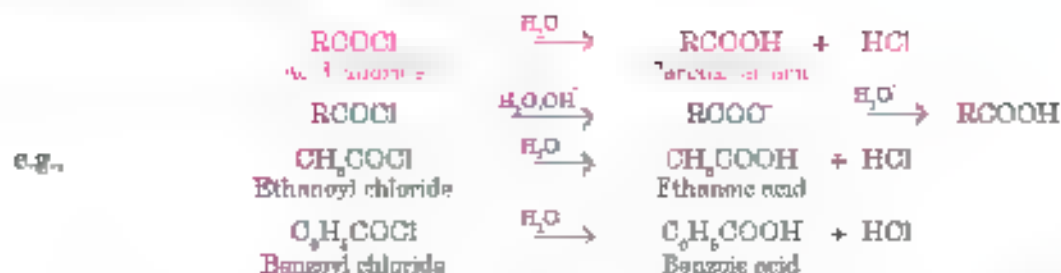


4. From Grignard reagents. Carboxylic acids can be prepared by the action of Grignard reagents on carbon dioxide (dry ice). The reaction is carried out in ethereal solution of suitable Grignard reagent and CO₂. It first forms salts of carboxylic acid which on treatment with mineral acids to corresponding carboxylic acids. For example,

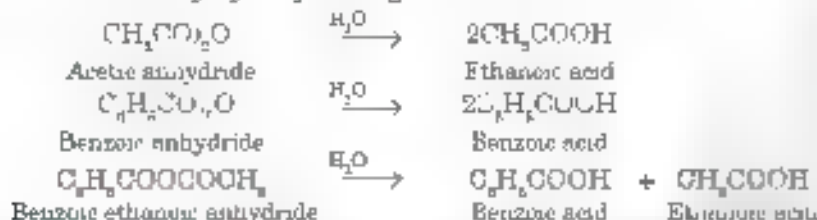


It may be noted that the acid formed by this method contains one more carbon atom than the original Grignard reagent.

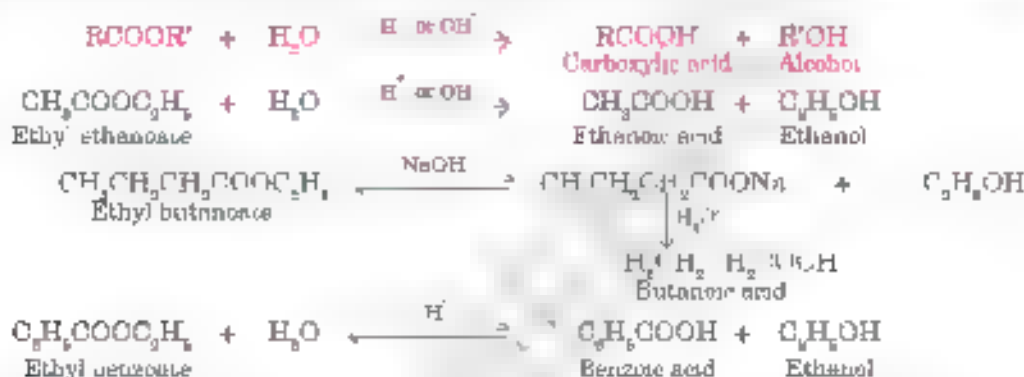
5. From acyl halides and anhydrides. Acid chlorides on hydrolysis with water give carboxylic acids. These are readily hydrolysed with aqueous base to form carboxylate ions which on acidification give corresponding carboxylic acids.



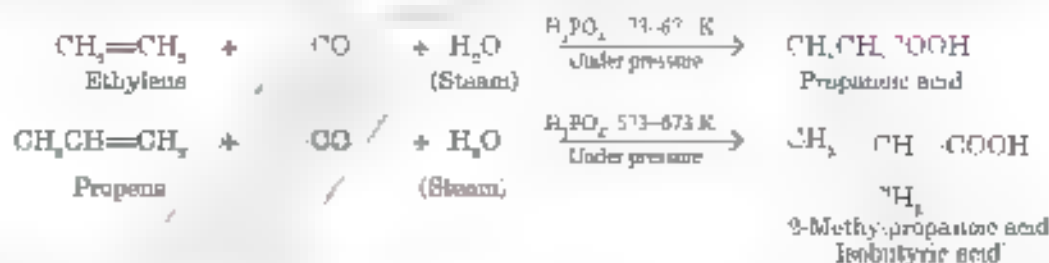
Acid anhydrides are also easily hydrolysed to give acids.



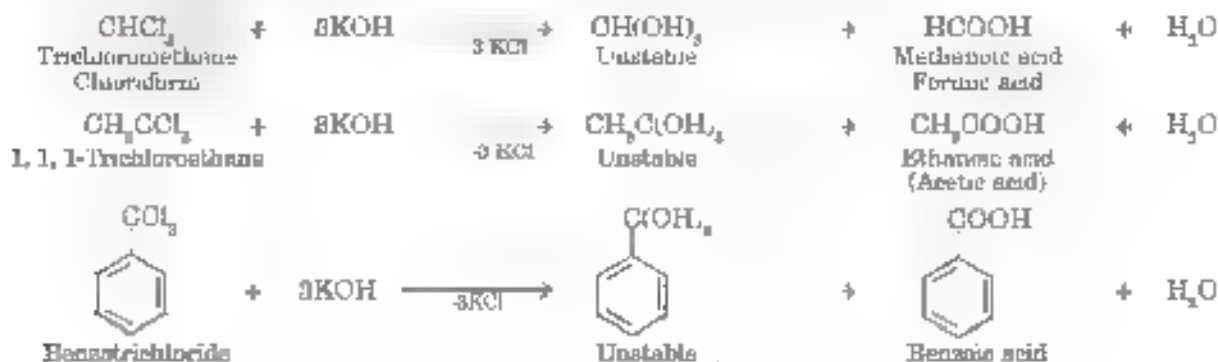
6. By hydrolysis of esters. Carboxylic acids can also be obtained by the hydrolysis of esters with mineral acids or alkalis. Acidic hydrolysis of esters gives directly carboxylic acids while alkaline hydrolysis gives carboxylates, which on acidification give corresponding carboxylic acids. For example,



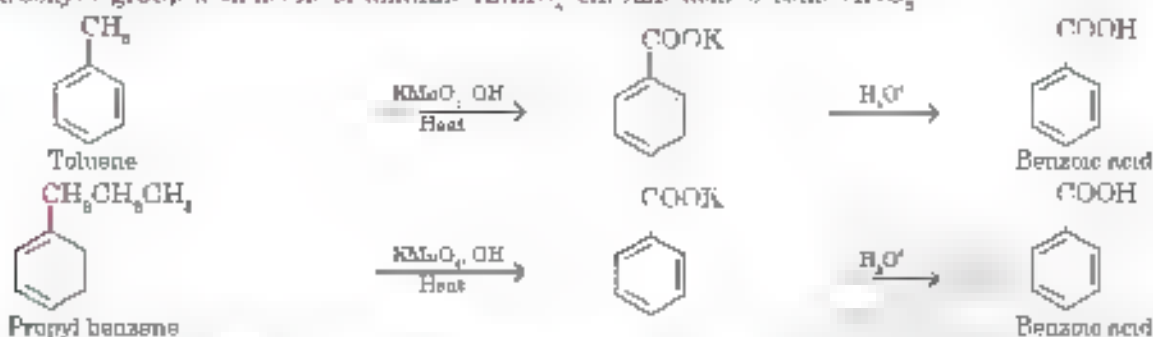
7. Carboxylation of alkenes. Carboxylic acids are obtained on a large scale by reacting alkenes with CO and steam under pressure with phosphoric acid at 573–673 K. This reaction is called **Koch reaction**.



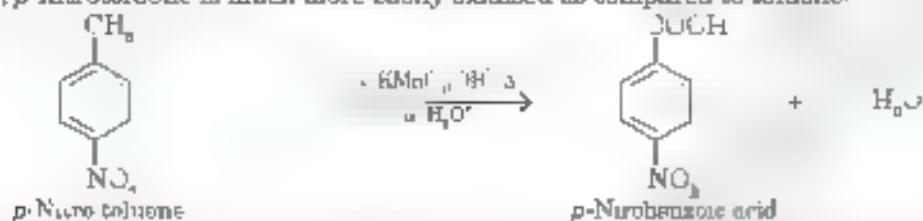
8. From trihalogen derivatives of hydrocarbons. Carboxylic acids can be prepared by the hydrolysis of 1, 1, 1-trihalogen derivatives of alkanes or arylhalides with aqueous KOH . For example,



9 Preparation of aromatic acids from alkyl benzenes. The alkyl side chain of benzene ring can be easily oxidised to carboxylic group with acidic or alkaline KMnO_4 , chromic acid or conc. HNO_3 .

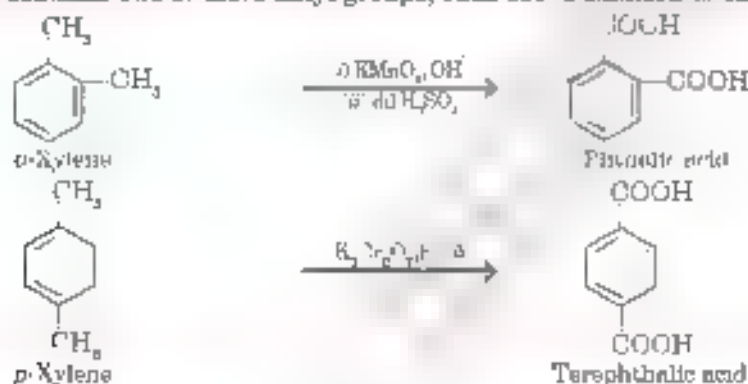


Presence of electron withdrawing groups on the benzene ring increases the reactivity of the benzylic hydrogens. For example, *p*-nitrotoluene is much more easily oxidised as compared to toluene.



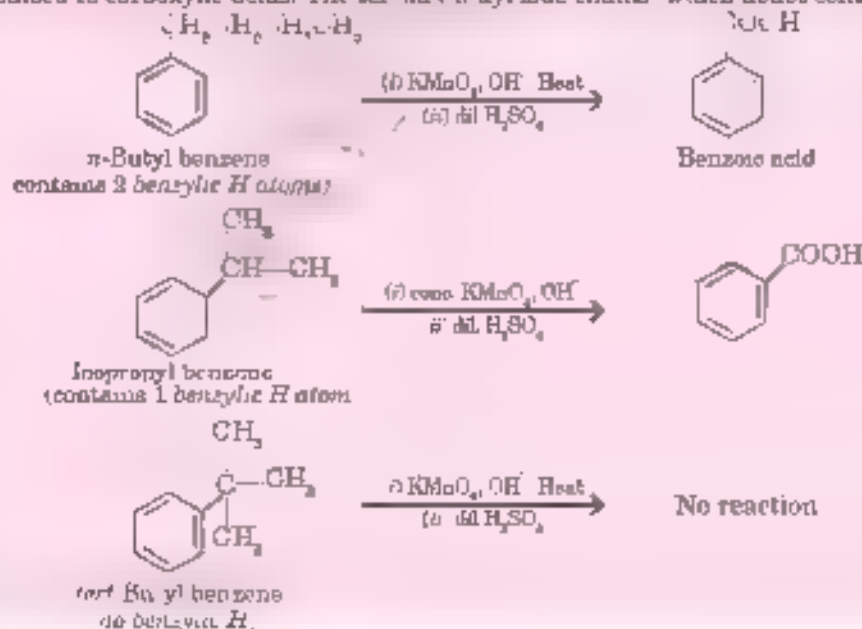
It may be noted that the complete side alkyl chain gets oxidised to COOH group irrespective of the length of the chain.

If the ring contains two or more alkyl groups, each one is oxidised to carboxyl group.



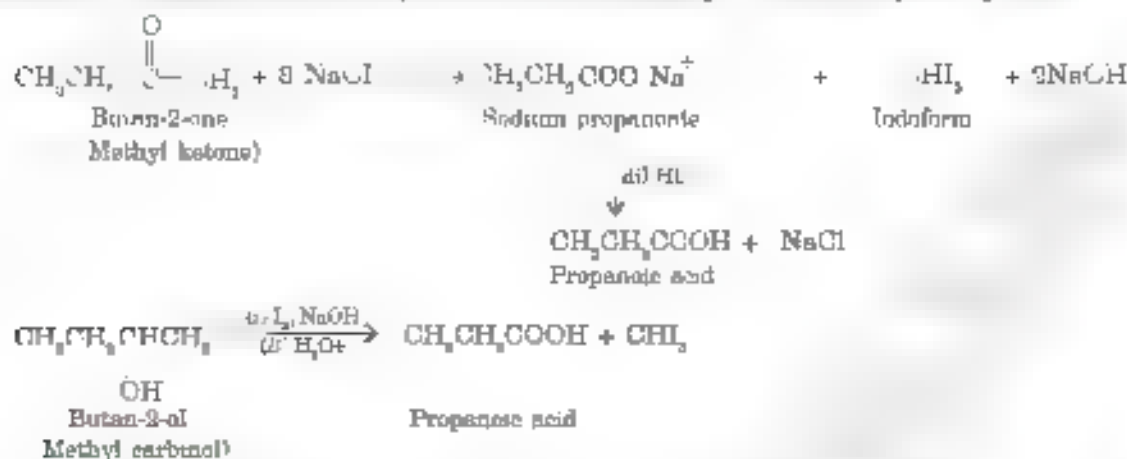
NOTE

It may be noted that only primary and secondary alkyl side chains on the benzene ring i.e. those containing benzylic hydrogens are oxidised to carboxylic acids. The tertiary alkyl side chains which do not contain benzylic hydrogen are not oxidised.

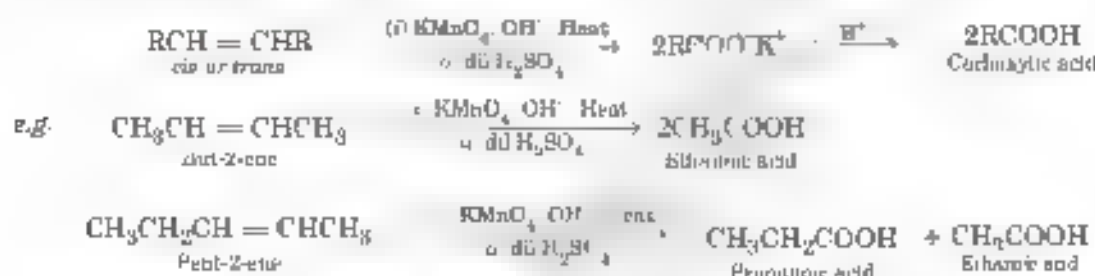


It may be concluded that larger the number of H atoms greater is the ease of oxidation. Thus, the ease of oxidation of different alkyl side chains follows the order $1^\circ > 2^\circ > 3^\circ$

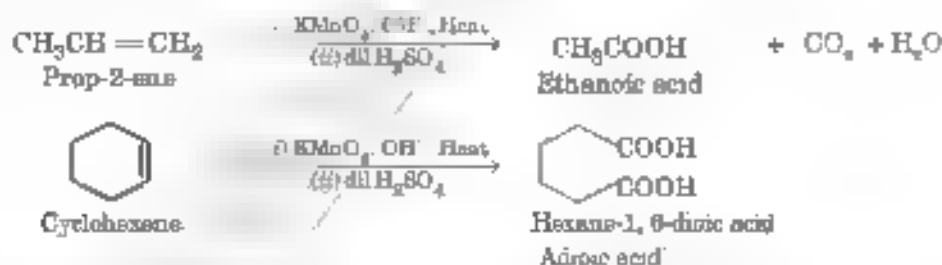
10 From methyl ketones or methyl carbinols Methyl ketones or methyl carbinols on treatment with a solution of sodium hypohalite (NaOI , NaOBr or NaOCl) undergo haloform reaction to form corresponding haloform (CHI_3 , CHBr_3 or CHCl_3) and sodium salt of carboxylic acids containing one carbon atom less than the parent methyl ketone or methyl carbinol. The sodium salt of carboxylic acid on acidification gives the corresponding acids.



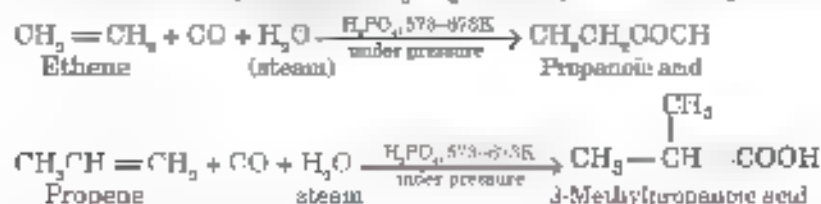
11 Oxidation of alkenes. Alkenes can also be cleaved by oxidizing agents such as hot acidic KMnO_4 or $\text{K}_2\text{Cr}_2\text{O}_7$ solution. For example, substituted alkenes give only acids.



The terminal CH_3 group of a 1-alkene is completely oxidized to CO_2 and water while disubstituted carbon atom of double bond becomes the $>\text{C}=\text{O}$ group of a ketone.



Monocarboxylic acids can also be prepared by heating an alkene with carbon monoxide and steam under pressure at 573–673K in the presence of H_3PO_4 as catalyst. For example,

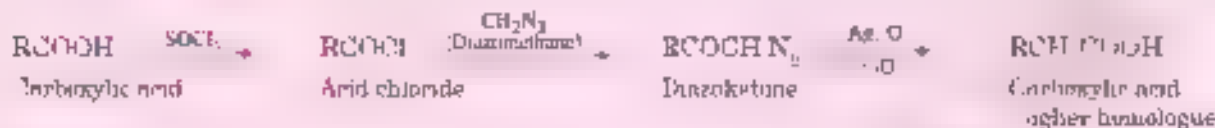


This reaction is called **Koch's reaction**.

12. By passing carbon monoxide on heated sodium alkoxide. Carbon monoxide is passed over heated suitable sodium alkoxide under pressure to form sodium salt of the carboxylic acid, which upon subsequent acidification gives the corresponding acid.



An acid RCOOH can be converted into its next higher homologue RCH_2COOH by a method known as **Arndt-Eistert synthesis**. This conversion is also called **homologation of an acid**. It involves the following steps:

[illegible]

The conversion of diazoketone to ketone upon heating with Ag is known as **Wolff rearrangement**.

□ **Example 16.**

How will you convert the following ? Give chemical equations :

- (i), Butan-1-ol to butanoic acid
- (ii), Cyclohexene to Hexane-1, 6-dioic acid
- (iii), Benzyl alcohol to phenyl ethanoic acid
- (iv), 4-Methyl acetophenone to benzene-1, 4-dicarboxylic acid
- (v), 3-Nitrobromobenzene to 3-nitrobenzoic acid
- (vi), Butanal to butanoic acid

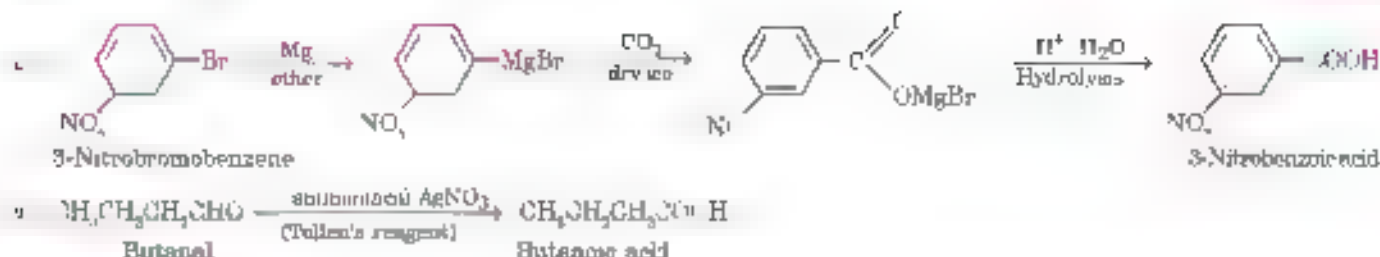
FIGURE 2

(i) $\text{CH}_3(\text{CH}_2)_3\text{CH}_2\text{OH} \xrightarrow[\text{Jones reagent}]{\text{CrO}_3, \text{H}_2\text{SO}_4, \text{H}^+} \text{CH}_3(\text{CH}_2)_3\text{COOH}$
 Butan-1-ol Butanoic acid

(ii) $\text{C}_6\text{H}_{10} \xrightarrow[\text{H}_2\text{SO}_4, \text{Heat}]{\text{KMnO}_4} \text{HOOC(CH}_2)_4\text{COOH}$
 Cyclohexene Hexane-1,6-dioic acid (adipic acid)

(a) $\text{C}_6\text{H}_5\text{CH}_2\text{OH} \xrightarrow[\text{or PBr}_3]{\text{HBr}} \text{C}_6\text{H}_5\text{CH}_2\text{Br} \xrightarrow{\text{KCN}} \text{C}_6\text{H}_5\text{CH}_2\text{CN} \xrightarrow[\text{H}_3\text{O}^+]{\text{H}^+/\text{H}_2\text{O}} \text{C}_6\text{H}_5\text{CH}_2\text{COOH}$
 Benzyl alcohol Benzyl bromide Benzyl cyanide Phenylethanoic acid

(b) $\text{C}_6\text{H}_4(\text{CH}_3)(\text{COCH}_3) \xrightarrow[\text{Ruh}]{\text{KMnO}_4} \text{KOCOC}_6\text{H}_4\text{COOK} \xrightarrow{\text{H}^+} \text{HOOC-C}_6\text{H}_4\text{-COOH}$
 4-Methyl acetophenone Dipotassium benzene-1,4-dicarboxylate Benzene-1,4-dicarboxylic acid (terephthalic acid)



Practice Problems

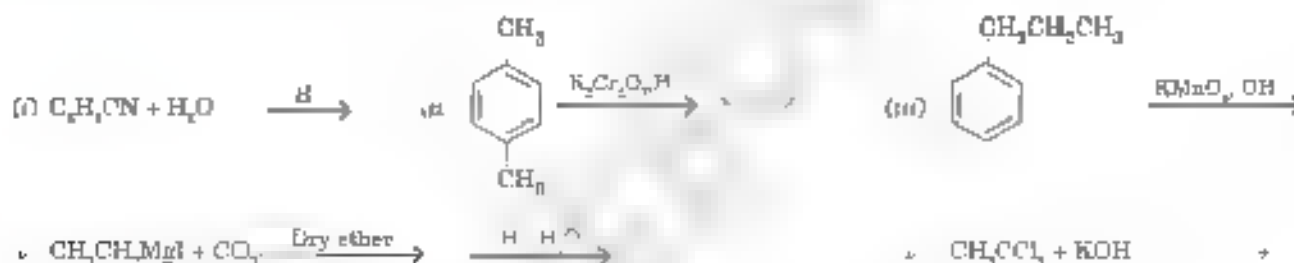
25. Write equations for the preparation of benzoic acid from the following compounds

- i) benzyl alcohol (ii) toluene
 iii) benzonitrile (iv) ethyl benzene
 v) benzene trichloride

26. How will you prepare

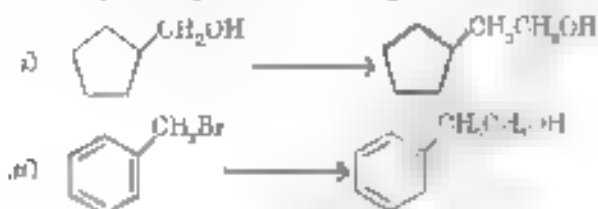
- i) acetic acid from acetylene (ii) butanoic acid from 1-propanol
 iii) benzoic acid from ammonia (iv) ethanoic acid from carbon dioxide

27. Complete the following reactions indicating the major product formed

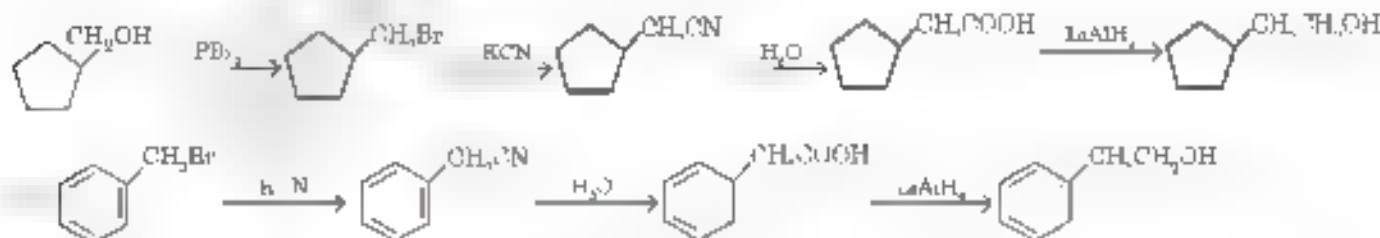


- Ans. i) Benzoic acid (ii) Terephthalic acid (iii) Benzoic acid
 iv) Propanoic acid (v) Acetic acid

28. How would you carry out the following transformations?



● Ans.



PHYSICAL PROPERTIES OF CARBOXYLIC ACIDS

The important physical properties of carboxylic acids are given below

1 Physical state. The first three members of the carboxylic acids are colourless liquids and have pungent smell. The next six members are oily liquids with a faint unpleasant odour. Thereafter, they are colourless waxy solids. Benzoic acid and its homologues are colourless solids.

2. Solubility Among the aliphatic acids, the first four members are very soluble in water and the solubility decreases gradually with the rise in molecular mass. However, all are soluble in alcohol or ether. Benzoic acid is sparingly soluble in cold water but is soluble in hot water, alcohol, ether.

The solubility of lower members of carboxylic acids is due to the hydrogen bonding in which the carboxylic oxygen forms hydrogen bonds with H atoms of water and hydroxylic H atoms. $-OH$ form hydrogen bonds with oxygen atom of water as shown alongside.

The solubility of carboxylic acid gradually decreases with the increase in size of the alkyl group or molecular mass. This is due to reduced polarity and hindrance provided by large bulky groups to the carboxylic group for taking part in hydrogen bonding. For example pentanoic acid and hexanoic acid are only slightly soluble in water. But the higher members are practically insoluble in water.

Aromatic acids are almost insoluble in water. Benzoic acid, for example, the simplest aromatic carboxylic acid is nearly insoluble in cold water. However, it is sufficiently soluble in hot water. Both aliphatic and aromatic carboxylic acids are soluble in less polar organic solvents such as benzene, ether and alcohol.

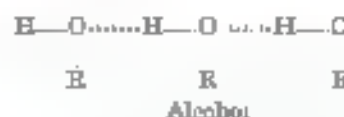
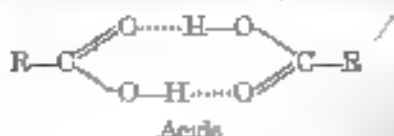
3 Boiling points. The carboxylic acids have higher boiling points due to the presence of intermolecular hydrogen bonding. As a result of hydrogen bonding, they exist as dimers. The hydrogen bonds are not broken completely even in the vapour phase. In fact, most carboxylic acids exist as dimers in the vapour phase and in aprotic solvents. They have higher boiling points than the corresponding aldehydes, ketones and even alcohols of comparable molecular masses.

For example, the boiling point of ethanoic acid is 391 K, whereas that of propanol is 370 K, both have molecular mass 60.

Compound	CH_3COOH Acetic acid 60 K	$CH_3CH_2CH_2OH$ n-Propyl alcohol 60 K	CH_3CH_2CHO Propionaldehyde 58 K	CH_3COCH_3 Acetone 58 K	$CH_3CH_2CH_2CH_3$ n-Butane 28 K
Boiling point					

The higher boiling points of carboxylic acids compared to alcohols is due to the following reasons:

- As compared to alcohols, the $O-H$ bond in carboxylic acids is more strongly polarised due to the presence of adjacent electron withdrawing carbonyl group. Therefore, carboxylic acids can form stronger hydrogen bonds.
- The molecules of carboxylic acids are held together by two hydrogen bonds and therefore, form cyclic dimers.



Thus, the carboxylic acid molecules are held together by strong attractive forces and therefore, they have higher boiling points. The existence of cyclic dimers of carboxylic acids is supported by the fact that the observed molecular masses in solvents are quite higher, almost double than their actual values. For example, the molecular mass of acetic acid in benzene as determined by measurement of colligative properties such as depression in freezing point is 120 instead of 60. This shows that acetic acid exists as dimer in benzene.

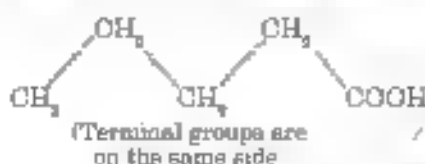
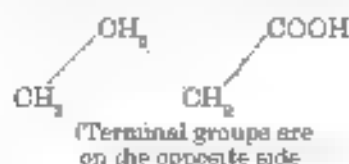
Among the monocarboxylic acids, the boiling points increase with increase in the molecular mass. As the size of the alkyl group increases, the magnitude of the attractive forces, which are the van der Waals forces, increases and therefore boiling points increase. For example,

Acid	$HCOOH$	CH_3COOH	C_2H_5COOH	C_3H_7COOH
Boiling point	375 K	391 K	424 K	437 K

4 Melting points. The melting points of carboxylic acids increase irregularly with increase of molecular mass. It has been observed that for the first ten members, the melting points of carboxylic acids containing even number of carbon atoms is higher than the next lower and higher member containing odd number of carbon atoms. For example,

Acid	CH_3CH_2COOH (3 carbons)	$CH_3CH_2CH_2COOH$ (4 carbons)	$CH_3CH_2CH_2CH_2COOH$ (5 carbons)
Melting point	26°	26°	27°

The X ray diffraction studies have shown that the acids with even number of carbon atoms have carboxyl group and terminal methyl group on the opposite sides of the zig-zag carbon chain. As a result, they fit into the crystal lattice better and results in stronger intermolecular forces. On the other hand, the acids with odd number of carbon atoms have carboxyl and terminal methyl groups on the same side of the zig-zag carbon chain. Therefore, these fit in the crystal lattice poorly and, hence, have weaker intermolecular forces. Thus, because of stronger intermolecular forces, the melting points of carboxylic acids with even number of C atoms are higher than those of odd number of C atoms above and below it. This trend is, however, noticed only in members having up to ten carbon atoms, in higher members the melting points generally increase with increase in molecular masses.



The melting and boiling points of aromatic acids are usually higher than those of aliphatic acids of comparable molecular masses. This is probably due to the fact that benzene has planar ring which can pack closely in the crystal lattice than zig-zag structure of aliphatic acids.

CHEMICAL PROPERTIES OF CARBOXYLIC ACIDS

The main chemical characteristics of carboxylic acids may be discussed under the following heads:

A. Reactions due to hydrogen atom of carboxyl group.

B. Reactions due to OH part of carboxyl group.

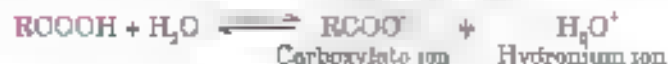
C. Reactions due to carboxyl group.

D. Reactions due to alkyl group and benzene ring.

A. Reactions due to hydrogen atom of the carboxyl group (involving cleavage of O—H bond)

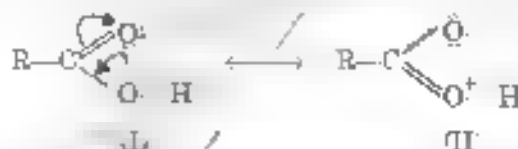
1. **Acidic character.** Carboxylic acids are generally acidic. They ionize in water to give hydronium ion

38



However, the acidic strength of carboxylic acids is much less than that of the mineral acids. The strength of the acid depends upon the extent of ionization, which in turn depends upon the stability of the anion formed. Carboxylic acids are acidic because the carboxylate ions formed are stable and hence, carboxylic acids have greater tendency to ionize to form stable carboxylate ions. This may be understood as follows:

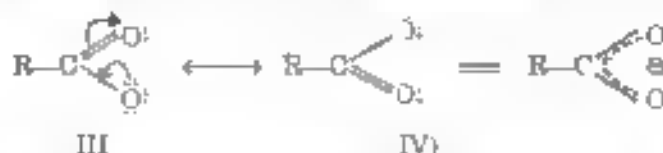
The carboxylic acid molecule is resonance hybrid of the following two structures.



It is clear that in the resonance hybrid structure II, the oxygen atom of the hydroxyl group carries some positive charge. Consequently, the electron pair of the O—H is displaced towards oxygen atom. This displacement of electrons causes the release of a proton and a carboxylate ion, RCOO^- is formed.



The carboxylate ion thus formed is also a resonance hybrid of structures III and IV as shown below:



Thus, we observe that carboxylic acid as well as its anion are resonance stabilised. However, if we compare these structures, we observe that resonance is less important for the acid than for the carboxylate ions.

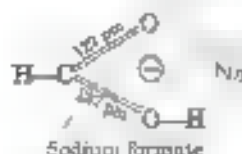
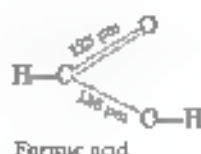
The contributing structures of carboxylic acid are not equivalent and therefore, these may be of different stability. On the other hand, the contributing structures of carboxylate ion are equivalent and therefore, these must be of equal stability. These equivalent structures of carboxylate ion contribute to its greater stability as compared to that of carboxylic acid molecule.

→ The contributing structures of carboxylate ion have only negative charge, whereas those for carboxylic acid have positive and negative charge. Since energy must be supplied to separate opposite charges and therefore, structure II should contain more energy and therefore less stable than I.

Therefore, the carboxylate ion is more resonance stabilized than the carboxylic acid. Thus, the carboxylic acids readily give a proton to form stable carboxylate ion.



The resonance in carboxylate ion is also supported by the bond length values. In carboxylic acid, there is one carbon-oxygen double bond and one single bond. Therefore, we expect these bonds to have different bond lengths. In the other hand, in carboxylate ion, there is resonance between two equivalent structures and therefore, we expect the two carbon-oxygen bonds to be of equal bond lengths. This is expected to have bond length between double and single bonds. The above conclusion is supported by X-ray and electron diffraction studies. For example, in formic acid the bond lengths are 136 pm (single bond) and 128 pm (double bond). In the other hand, in sodium formate containing formate ion, two carbon-oxygen bond lengths are same, 127 pm each, which lie between the values of C—O and C=O bond lengths. Carboxylic acids readily give proton to form stable carboxylate ion.



The stability of carboxylate ion can also be understood in terms of **delocalisation** of the π -electron density. The carbonyl carbon involves sp^2 hybridisation (leaving one unhybridised p -orbital). This p -orbital can overlap sidewise with either of the p -orbital of oxygen atom forming π bond (Fig. a and b). The resulting π -orbital cloud is spread over both oxygen atoms and carbon atom. This **delocalisation** gives stability to the carboxylate ion.



Expressing strength of carboxylic acids. The carboxylic acids are acidic. However, they are much weaker acids than the mineral acids. The strength of carboxylic acid can be expressed in terms of the dissociation constant K_a as,



$$K_a = \frac{[\text{RCOO}^-][\text{H}_3\text{O}^+]}{[\text{H}_2\text{O}][\text{RCOOH}]}$$

$$\text{or } K_a = K_w [\text{H}_2\text{O}] = \frac{[\text{RCOO}^-][\text{H}_3\text{O}^+]}{[\text{RCOOH}]}$$

Where K_w is equilibrium constant and K_a is the dissociation constant

The dissociation constant is generally called **acidity constant** because it measures the relative strength of an acid. The stronger the acid, the larger will be its K_a value.

The dissociation constant of an acid can also be expressed in terms of pK_a which is defined as

$$pK_a = -\log K_a$$

Now a stronger acid will have higher K_a value but smaller pK_a value while a weaker acid will have smaller K_a value but higher pK_a value. In other words

Larger the value of pK_a , weaker the acid is.

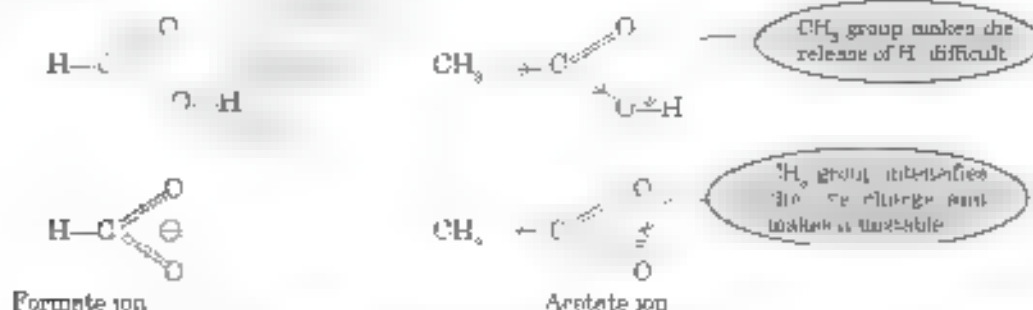
The K_a and pK_a values of some acids are given below

Acid	K_a	pK_a	Acid	K_a	pK_a
HCOOH	1.77×10^{-4}	3.75	C_6H_5COOH	1.3×10^{-5}	4.90
H_2CO_3	7×10^{-8}	4.76	$p\text{-NO}_2C_6H_4COOH$	10×10^{-4}	3.44
FCH_2COOH	100×10^{-4}	2.50	$m\text{-NO}_2C_6H_4COOH$	21×10^{-4}	3.50
$ClCH_2COOH$	1.36×10^{-3}	2.87	$o\text{-NO}_2C_6H_4COOH$	871×10^{-6}	2.17
$BrCH_2COOH$	25×10^{-4}	2.9	$p\text{-CH}_3C_6H_4COOH$	4.2×10^{-5}	4.38
ICH_2COOH	6×10^{-4}	3.10	$m\text{-CH}_3C_6H_4COOH$	6.4×10^{-5}	4.2
$Cl_2CHCOOH$	6630×10^{-6}	1.28	$o\text{-CH}_3C_6H_4COOH$	1.24×10^{-5}	5.01
Cl_3CCOOH	29200×10^{-6}	0.53	$o\text{-OH}C_6H_4COOH$	105×10^{-6}	2.98
$CH_3CH_2CH_2ClCOOH$	130×10^{-5}	2.88	$m\text{-OH}C_6H_4COOH$	8.3×10^{-6}	4.08
$H_2C(OH)CH_2COOH$	80×10^{-6}	4.05	$p\text{-OH}C_6H_4COOH$	2.6×10^{-6}	4.58

In general, strong acids have pK_a values < 1 , the acids with pK_a values between 1 and 5 are considered to be moderately strong acids, weak acids have pK_a values between 5 and 10 and extremely weak acids have pK_a values > 15 .

Effect of substituents on acidic strength of acids. The substituents have a marked effect on the acidic strength of carboxylic acids. The nature of substituents affects the stability of the conjugate base (carboxylate ion) and hence affects the acidity of the carboxylic acids. In general, electron withdrawing groups (EWG) increase the stability of the carboxylate ion by delocalising the negative charge and hence increase the acidity of the carboxylic acid. Conversely, electron donating groups (EDG) decrease the stability of the carboxylate ion by intensifying the negative charge and hence decrease the acidity of the carboxylic acid. This is discussed below.

(a) Electron donating (or releasing) substituents. Alkyl is an electron releasing group. If the H atom of formic acid is replaced by CH_3 group to form acetic acid (CH_3COOH) the alkyl group will tend to increase the electron density on the oxygen atom of the $O-H$ bond. Consequently, the release of H^+ ion in acetic acid will be more difficult as compared to formic acid. Apart from this, the methyl group will also destabilise the acetate ion by intensifying the negative charge relative to the formate ion.



Thus, the release of H^+ ion from acetic acid will be difficult as compared to formic acid or the former is a weaker acid. In general, greater the +I effect of the alkyl group attached to the carboxyl group, lesser will be the acidic strength of the carboxylic acid. The +I effect of the alkyl groups increase in the order



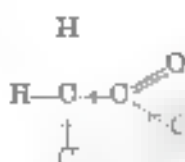
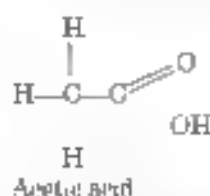
Therefore, acetic acid CH_3COOH is a stronger acid than propionic acid $\text{CH}_3\text{CH}_2\text{COOH}$ which is still stronger than isobutyric acid $(\text{CH}_3)_2\text{CHCOOH}$ and so on.



Acidic strength decreases

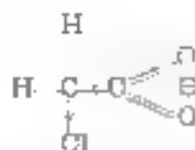
(b) Electron withdrawing substituents. The electron withdrawing substituents such as halogen atom will tend to withdraw the electron charge when attached to the carboxylic acid at a specific position. Consider the example of chloroacetic acid.

Chlorine is an electron attracting atom (inductive effect). It withdraws the electrons from the carbon to which it is attached and this effect is transmitted throughout the chain. As a result the electrons are withdrawn more strongly towards oxygen of $\text{O}-\text{H}$ bond and promotes the release of proton. Consequently, acidic strength increases. Therefore, *chloroacetic acid is stronger acid than acetic acid.*



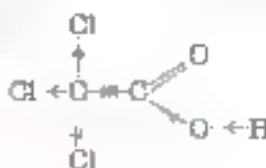
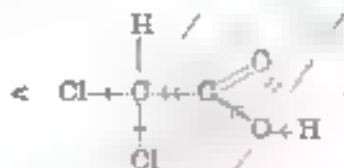
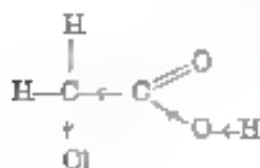
Cl makes the release of H^+ easy

Further, because of electron withdrawing tendency of Cl atom, inductive effect stabilises the carboxylate anion by dispersing the negative charge and therefore, strengthening the acid.



Cl atom stabilises the anion by dispersal of charge

(c) Effect of number of halogen atoms. The inductive effect increases with increase in number of chlorine atoms and therefore, acidic strength also increases.



Acidic strength increases

Thus, the acidic strength decreases in the order

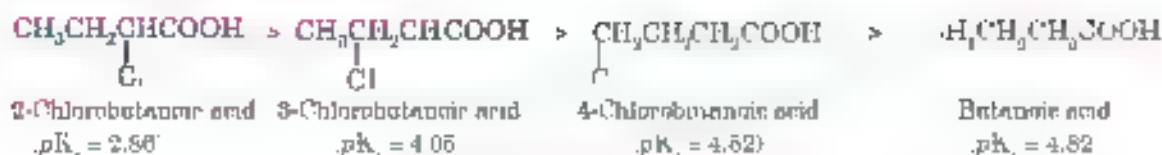


(d) Nature of halogen atom. The strength of carboxylic acid also depends upon the nature of the electron withdrawing halogen atom. Greater the electron withdrawing influence of the halogen atom, stronger will be the acid. For example, the electron withdrawing effect (inductive effect) of the halogen decreases in the order $\text{F} > \text{Cl} > \text{Br} > \text{I}$, therefore, the acidic strength of monocarboxylic acids decreases in the same order as



Acidic strength increases

(e) Position of the halogen atom. We know that inductive effect decreases rapidly with distance. Therefore, as the distance between the electron withdrawing group and the $-\text{COOH}$ group increases, the electron withdrawing influence decreases. Beyond a few methylene groups, the effect becomes negligible. For example,



Acidic strength increases

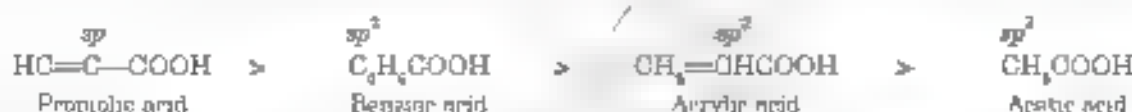
1e Effect of type of hybridisation of carbon atom bonded to $-\text{COOH}$ group.

Direct attachment of groups such as phenyl or vinyl to the carboxylic acid, increases the acidity of the corresponding carboxylic acid contrary to expected decrease because of resonance effect as shown below

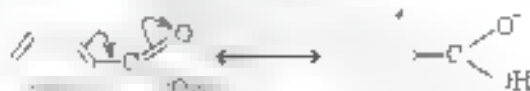


This is because of larger electronegativity of sp^2 hybridised carbon to which carboxyl group is attached.

In general, acidity increases as the electronegativity of the C atom directly attached to $-\text{COOH}$ group increases or the hybridisation of the C atom directly attached to $-\text{COOH}$ changes from $sp^3 \rightarrow sp^2 \rightarrow sp$. For example,



As observed, benzoic acid ($pK_a = 4.19$) is a stronger acid than acrylic acid ($pK_a = 4.25$) because the double bond of a benzene ring is less electron donating since this delocalisation destroys the aromatic character of benzene. Thus, benzoic acid is a stronger acid than acrylic acid.



Similarly, benzoic acid is more acidic than acetic acid because in benzoic acid, $-\text{COOH}$ is attached to sp^2 C atom of the phenyl ring while in acetic acid, $-\text{COOH}$ is attached to sp^3 C atom of methyl group. However, formic acid does not contain any alkyl group and therefore, it is stronger acid ($pK_a = 2.75$) than benzoic acid. Thus, the relative acid strength of these three acids is



However, when a phenyl group is attached to a $-\text{COOH}$ group through one or more saturated carbon atoms, phenyl group has a weak electron withdrawing inductive effect. Therefore, phenyl acetic acid ($pK_a = 4.31$) is slightly stronger acid than acetic acid ($pK_a = 4.76$).

Thus, in a nutshell

- the electron withdrawing substituents disperse the negative charge on carboxylate ion and stabilize it and thus, increase acidity
- the electron releasing substituents intensify the negative charge of the carboxylate ion, destabilize it and thus, decrease the acidity.

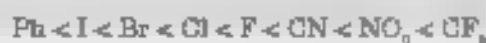


EWG withdraws electrons, stabilizes anion and strengthens acid



EDG releases electrons, destabilizes anion and weakens acid

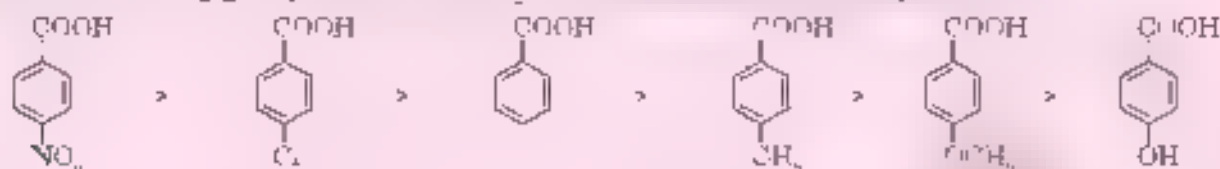
The effect of the following groups in increasing order of acidic strength is



Effect of Substituents on the Acidic Strength of Benzoic acid

Like aliphatic acids, the aromatic acids are also affected by the substituents as discussed below

The electron releasing groups like CH_3 , CH_3 , OCH_3 and NH_2 make benzoic acid **weaker** while electron withdrawing groups like Cl , NO_2 etc, make benzoic acid **stronger**. Thus,



The substituent effects on the acidic character of *p*-substituted benzoic acid, $\text{Y}-\text{C}_6\text{H}_4-\text{COOH}$ is given below

Electron releasing groups

Y	pK_a
OH	4.58
OCH_3	4.48
CH_3	4.38
NH_2	4.85

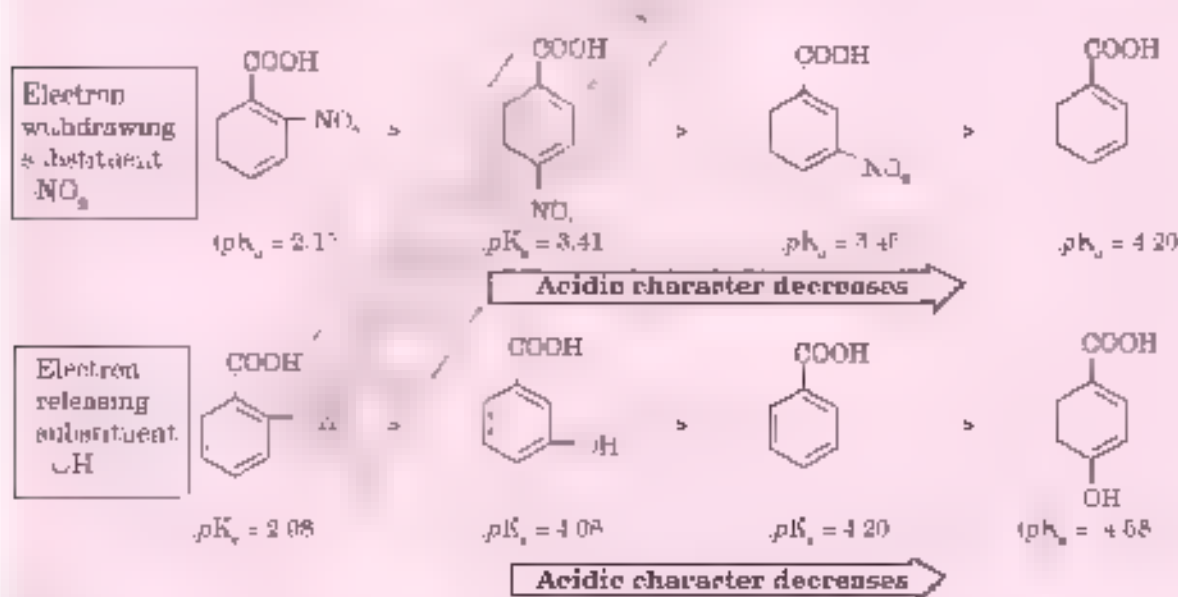
Electron withdrawing groups

Y	pK_a
Cl	4.0
Br	3.96
CHO	3.75
CN	3.55
NO_2	3.44

Benzoic acid $pK_a = 4.20$

The acid weakening effect of the electron donating groups and acid strengthening effect of the electron withdrawing groups is more pronounced at *p*-positions than at *m*-positions. Thus, among *p*- and *m*-isomers,

p-isomer has more acidic character than *m*-isomer for electron withdrawing group. In the other hand, for electron releasing group *p*-isomer is stronger acid than benzoic acid while *m*-isomer is weaker than benzoic acid. For example



The *ortho* isomer of *p*-ary substituted benzoic acid is the strongest acid among the three isomers, no matter whether the substituent is electron donating (e.g., CH_3 , H , NH_2 etc.) or electron withdrawing (e.g., Cl , NO_2 , CN , COCH_3 etc.). This effect is called **ortho effect**. It is mainly a combination of both steric and electronic factors. Discussion is beyond the scope of present class.

The effect of substituents on the acid strength can be explained on the basis of combined effect of inductive effect (I), resonance effect (R) and ortho effect. Some common examples of relative acid strength of *o*-, *m*- and *p*-acids as compared to benzoic acid are given below.

Electron donating groups

Toluic acids		>		>		>	
pK_a values	4.08		4.20		4.24		4.34

Hydroxybenzoic acids		>		>			
pK_a values	2.98		4.08		4.20		4.58

Aminobenzoic acid		>		>		>	
pK_a values	4.20		4.72		4.80		4.85

Methoxy benzoic acids		=		>		>	
pK_a values	4.09		4.09		4.20		4.46

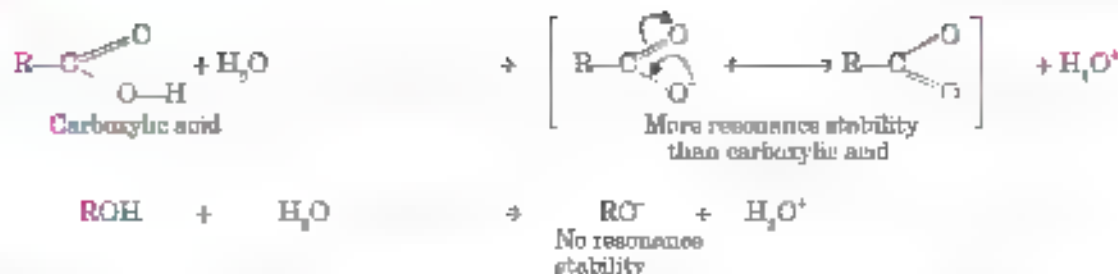
Electron withdrawing groups

Nitrobenzoic acids		>		>			
pK_a values	2.17		3.41		3.46		4.20

Chlorobenzoic acids		>		>			
pK_a values	2.84		3.83		3.89		4.20

Comparison of Relative Acidic Strength of Monocarboxylic Acids, Alcohols and Phenols

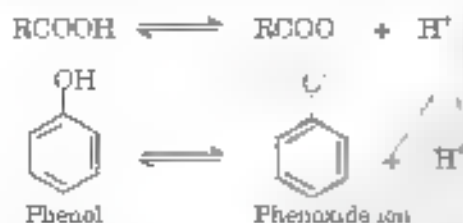
a) Carboxylic acids and alcohols. Monocarboxylic acids are stronger acids than the monohydric alcohols. This is due to the fact that both the carboxylic acids and the carboxylate ions are resonance stabilized and the carboxylate ion is more resonance stabilized in comparison to carboxylic acid. Therefore, carboxylic acids have tendency to give H^+ ion forming stable carboxylate ion. However, in alcohols no resonance is possible for the alcohol as well as alkoxide ion.



In fact, alcohols are very weak acids.

b. Carboxylic acids and phenols. Phenols are acidic because the phenoxide ion can be stabilised by delocalisation of negative charge into the ring. However phenols are less acidic (pK_a values) than carboxylic acids.

The difference in the relative acid strengths can be understood if we compare the resonance hybrids of carboxylate ion and phenoxide ion.

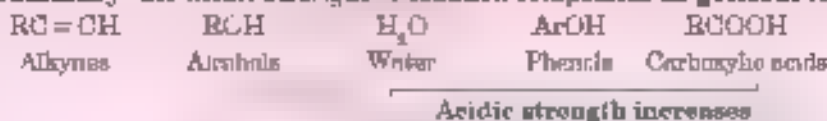


The resonance hybrids may be represented as

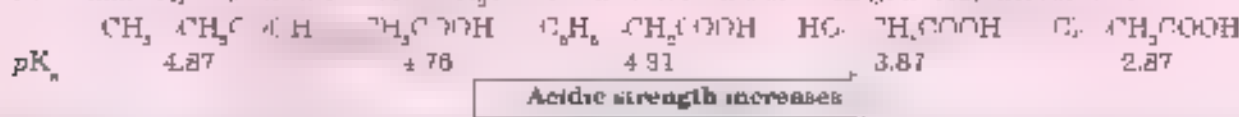


The electron charge in the carboxylate ion is more dispersed in comparison to the phenate ion since there are two electronegative oxygen atoms in carboxylate ion as compared to only one oxygen atom in phenate ion. Moreover, the carboxylate ion is stabilised by two equivalent resonance structures in which the negative charge is on the more electronegative oxygen atom. However phenoxide ion has non-equivalent resonance structures in which the negative charge is also on less electronegative carbon atom. Therefore resonance in phenoxide ion is not as important as it is in carboxylate ion. In other words, the carboxylate ion is relatively more stable as compared to phenate ion. Thus, the release of H^+ ion from carboxylic acid is comparatively easier or it behaves as a stronger acid than phenol.

In a **summary** the acidic strength of common compounds in general follows the order

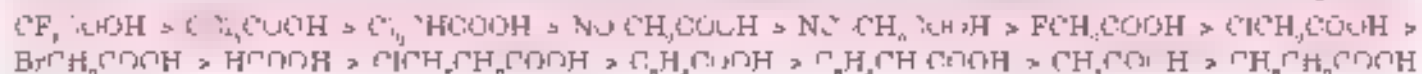


For common groups attached to $-\text{CH}_2\text{COOH}$ the acidic character in general, increases as



SUMUP

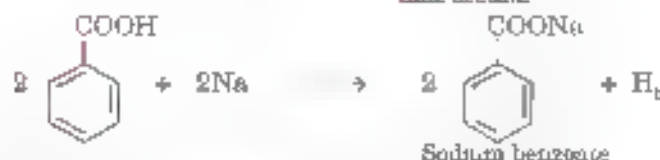
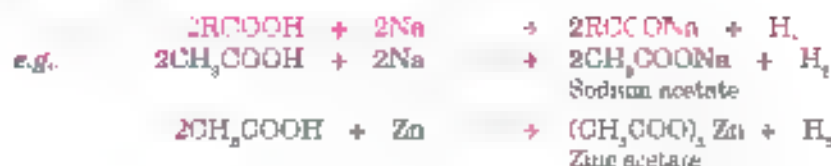
On the basis of above facts, the common acids are arranged in the following order of acidity based on their pK_a values.



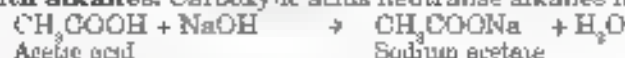
The acidic character of carboxylic acids can be shown by the following reactions:

1. **Action with blue litmus.** All carboxylic acids turn blue litmus red.

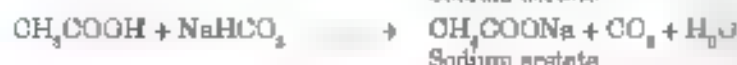
2. **Reaction with metals.** Carboxylic acids react with active metals such as Na, K, Ca, Mg, Zn, etc., to form their salts with the liberation of hydrogen.



3. Action with alkalis. Carboxylic acids neutralise alkalis forming salts and water



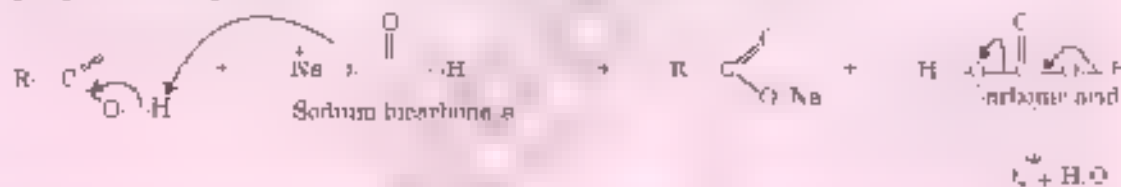
4. Action with carbonates and bicarbonates. Carboxylic acids decompose carbonates and bicarbonates evolving carbon dioxide with brisk effervescence



REMEMBER

Reaction of carboxylic acids with aqueous sodium carbonate and sodium bicarbonate evolves carbon dioxide with brisk effervescence. However, most phenols do not produce effervescence with aqueous solution of sodium carbonate. Therefore, this reaction may be used to distinguish between carboxylic acids and phenols.

It may be noted that during the reaction of carboxylic acids with Na_2CO_3 or NaHCO_3 , the carbon dioxide evolved comes from Na_2CO_3 or NaHCO_3 and not from carboxyl group as shown below



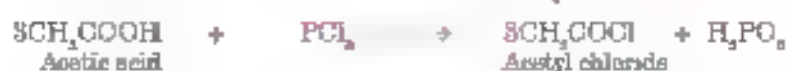
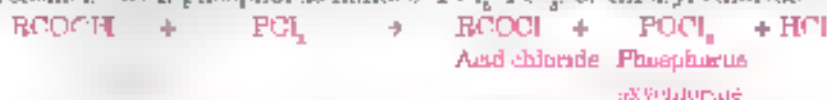
This is further supported by the observation that when ^{14}C labelled benzoic acid is treated with NaHCO_3 , unlabelled CO_2 is produced



E Reactions involving the $-\text{OH}$ group of the carboxylic acids involving cleavage of $\text{C}-\text{OH}$ bond

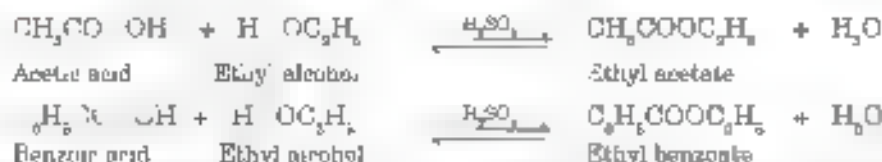
The $-\text{OH}$ group of carboxylic acids can be replaced by a number of groups such as $-\text{Cl}$, $-\text{OR}$, $-\text{NH}_2$ and $-\text{OOC}(\text{R})$ to form chlorides, esters, amides and anhydrides. These compounds are collectively called functional derivatives of carboxylic acids.

5. Formation of acid chlorides Reaction with PCl_5 , PCl_3 or SOCl_2 . Carboxylic acids can be converted into acid halides by treatment with phosphorus halides PCl_5 , PCl_3 or thionyl chloride SOCl_2 in pyridine. For example,





6. Formation of esters *Reaction with alcohols* When carboxylic acids are heated with an alcohol in the presence of concentrated H_2SO_4 or HCl esters are formed. The reaction is reversible in nature and is called **esterification**. For example,



The reaction is shifted to the right by using excess of alcohol or removal of water by distillation.

The rate at which a carboxylic acid is esterified depends primarily upon the steric hindrance in the alcohol and the carboxylic acid. The actual strength of carboxylic acids plays only a minor role in the rate of ester formation. Thus, the reactivity of alcohol towards esterification increases as



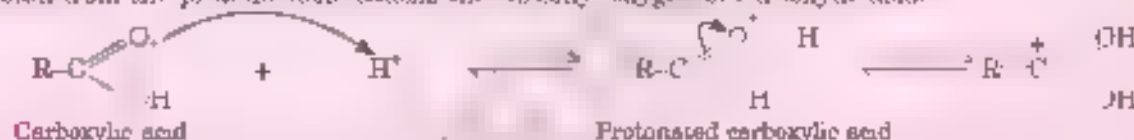
Similarly reactivity of carboxylic acid increases as



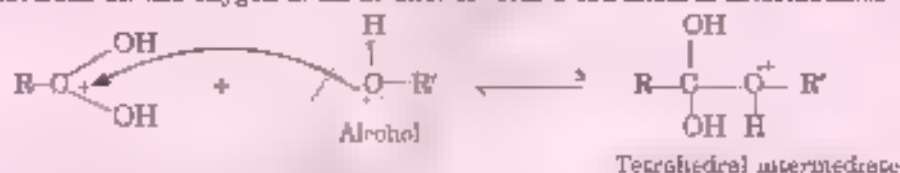
MECHANISM: ESTERIFICATION OF CARBOXYLIC ACIDS

The esterification of carboxylic acids with alcohols is a kind of nucleophilic acyl substitution reaction. The mechanism of esterification involves the following steps

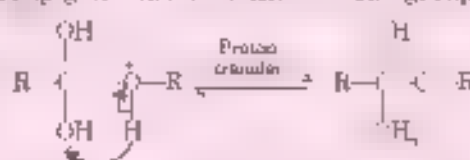
Step I A proton from the protonic acid attacks the carbonyl oxygen of carboxylic acid.



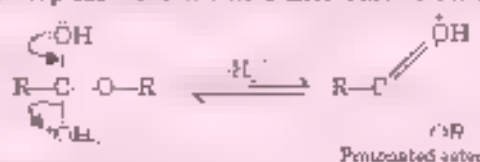
Step II As a result of protonation, the carbonyl carbon gets activated and hence readily undergoes attack by the lone pairs of electrons on the oxygen of an alcohol to form a tetrahedral intermediate.



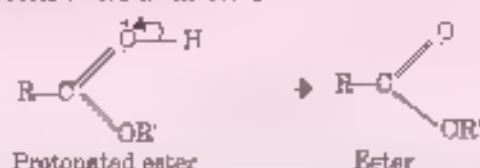
Step III From the resulting intermediate a proton shifts to OH group to form another tetrahedral intermediate. During this proton transfer the $-\text{H}$ group gets converted into $-\text{OH}_2^+$ group.



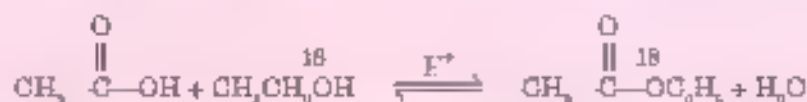
Step IV The intermediate formed in Step III uses a water molecule to form a protonated ester.



Step V The protonated ester loses a proton to form an ester.

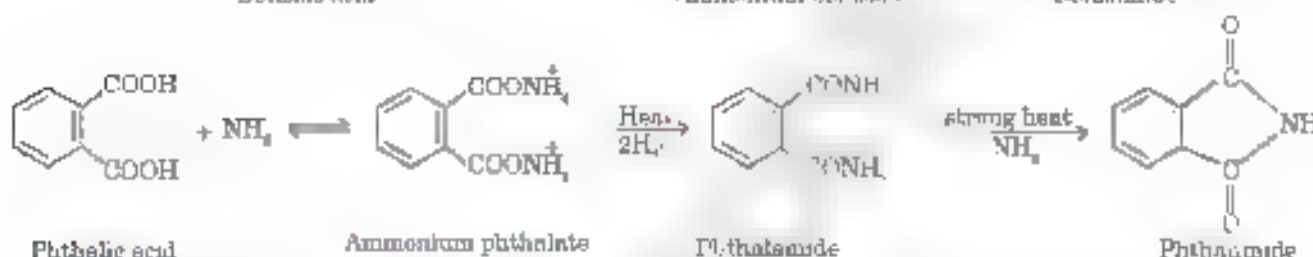
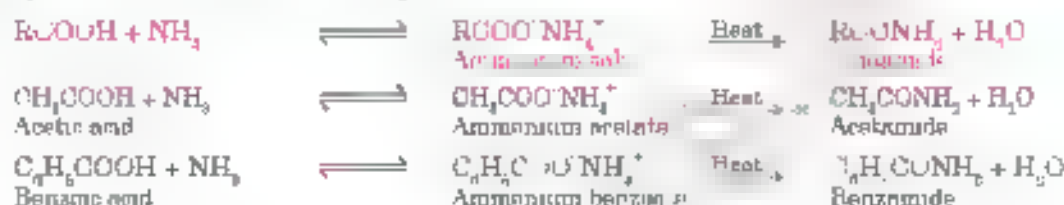


The mechanism is supported by the fact that acetic acid reacted with isotopically labelled ethanol $\text{CH}_3\text{CH}_2^{18}\text{OH}$ to give ethyl acetate having all the labelled oxygen in the ester while water did not contain any isotopic oxygen as

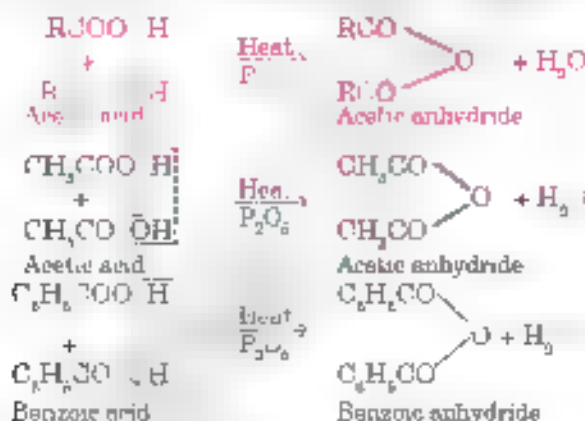


All the steps in the above mechanism are reversible.

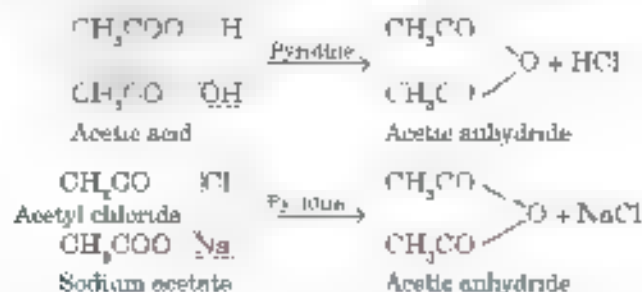
7 Formation of amides *Reaction with ammonia*: Carboxylic acids react with ammonia to form *ammonium salts* which upon heating form *acid amides*. For example,



8 Formation of acid anhydrides *Action of heat in the presence of P_2O_5* : Carboxylic acids on heating in the presence of a strong dehydrating agent such as phosphorus pentoxide, P_2O_5 or H_2SO_4 form corresponding acid anhydrides.



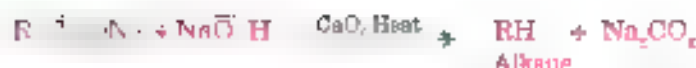
Acid anhydrides are also formed by treating acid chlorides with carboxylic acid in the presence of pyridine as a base or by treating acid chlorides with sodium salts of carboxylic acids.



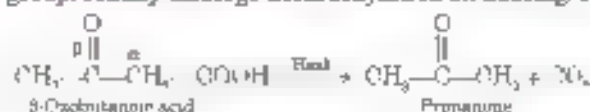
C : Reactions involving the carboxyl (-COOH) group

9. Decarboxylation: Carboxylic acids get decarboxylated, i.e. lose carbon dioxide under the following conditions

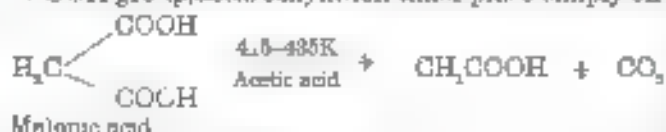
a) Sodium or potassium salts of carboxylic acids on heating with soda lime ($\text{NaOH} + \text{CaO}$) in the ratio of 3:1 give hydrocarbons which contain one carbon atom less than the parent acid.



It may be noted that carboxylic acids containing an electron withdrawing group such as Cl or NO_2 at β -carbon atom w.r.t the $-\text{COOH}$ group, readily undergo decarboxylation on heating. For example,



When two carboxylic groups are attached to the same carbon atom, gem dicarboxylic acids $\text{C}(\text{COOH})_2$ is present at β -carbon atom w.r.t $-\text{COOH}$ group, decarboxylation takes place easily on heating.

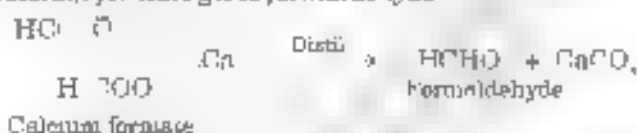


b. Electrolytic decarboxylation. Electrolysis of aqueous solutions of sodium or potassium salts of carboxylic acids undergo decarboxylation to give *alkanes*. This method is known as **Kolbe's electrolysis**.

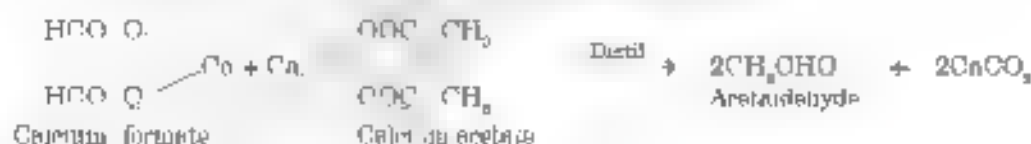


c. Decomposition of calcium salts of fatty acids. When calcium salts of carboxylic acids are heated *anhydrides* or *ketones* are formed. For example,

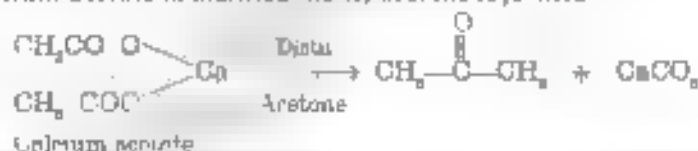
(i) *Distillation of calcium formate gives formaldehyde*



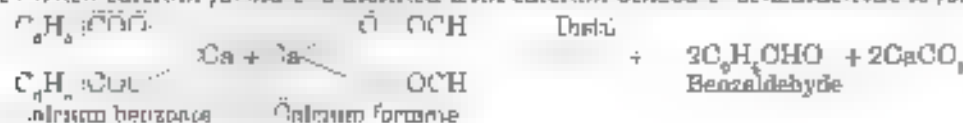
(ii) *When calcium formate is distilled with calcium acetate acetaldehyde is formed.*



(iii) *When calcium acetate is distilled alone, acetone is formed.*

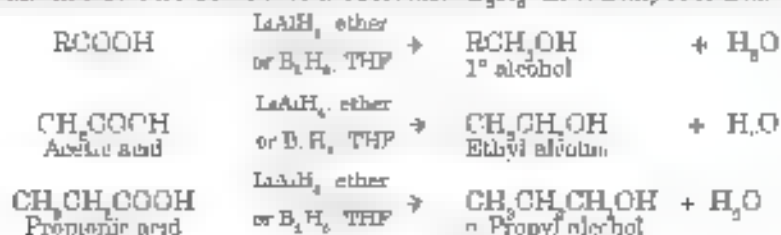


(iv) *When calcium formate is distilled with calcium benzoate benzaldehyde is formed*



10. Reduction

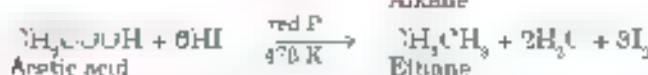
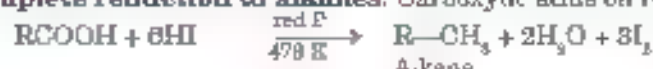
(a) **Partial reduction to alcohols.** Carboxylic acids on reduction with lithium aluminium hydride (LiAlH_4) or with hydrogen in the presence of copper chromite (CuCr_2O_4) are reduced to alcohols. Reduction of carboxylic acids to alcohols can also be carried out with diborane (B_2H_6) in tetrahydrofuran. This



NOTE

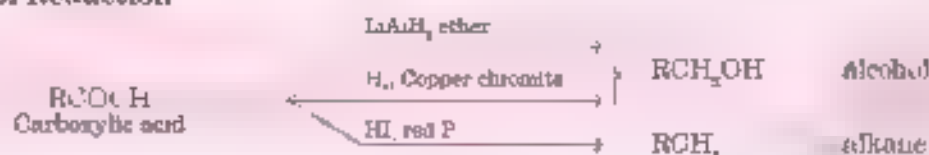
In these reactions, C of group of carboxylic group is reduced to CH_2 .

10.7 Complete reduction to alkanes. Carboxylic acids on reduction with HI and red P give alkanes.

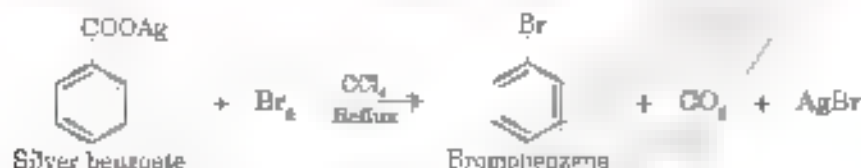
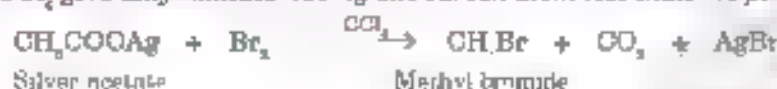


In the above reactions, the -COOH group is reduced to a CH_3 group.

Summary of Reduction



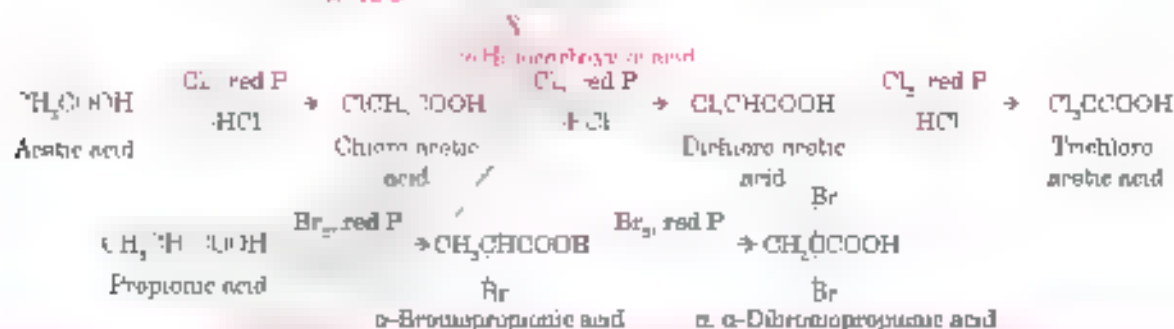
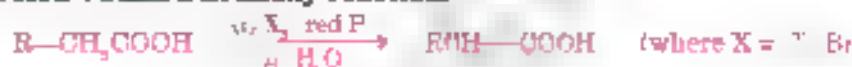
11. Action of bromine on silver salt of the acid. The silver salts of the carboxylic acid on treatment with Br_2 in the presence of CCl_4 give alkyl halides having one carbon atom less than the parent acid.



The reaction is called **Hunsdiecker reaction**.

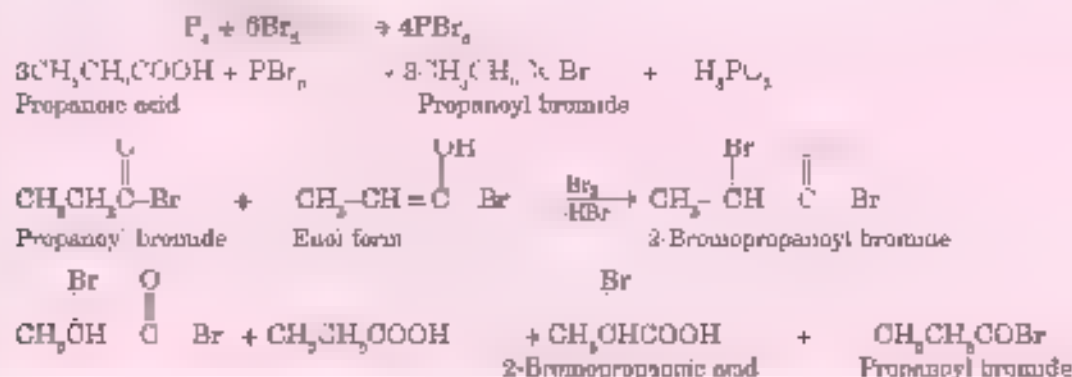
D : Reactions Involving Alkyl Group of Carboxylic Acids

12. Halogenation. Carboxylic acids having an α -hydrogen react with chlorine or bromine in the presence of a solution of red phosphorus to give compounds in which α -hydrogen atoms get replaced by halogen atoms. This reaction is called **Hofmann-Volhard-Zelinsky reaction**.



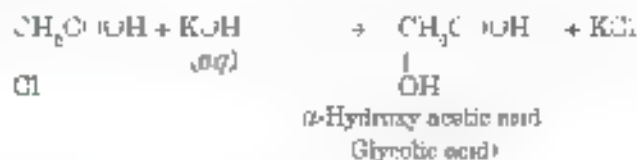
Function of red phosphorus

The function of red phosphorus is to first combine with bromine to form PBr_3 . This then reacts with carboxylic acid to form corresponding acid bromide which enolizes to a larger extent than the acid. Thus, it brings out α -bromination readily.



The halogen atom in monosubstituted acid can be easily replaced by a suitable atom or group to form a variety of compounds. Thus, α -halo acids are important synthetic intermediates. For example,

(i) *Action with aqueous KOH*

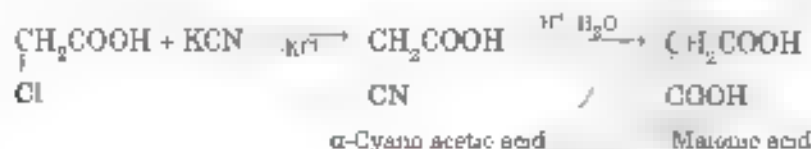


(ii) *Action with alcoholic ammonia*



Glycine exists as $\text{NH}_3^+ \text{CH}_2\text{COO}^-$ (dipolar ion)

(iii) *Action with potassium cyanide*

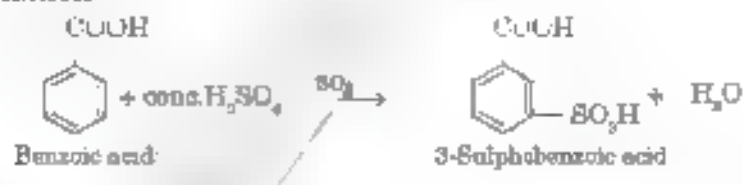


1.3 Ring substitution in aromatic acids Carboxyl group in benzoic acid is an electron withdrawing group and the carbon atom is an *ortho*-directing group. *Ortho* compounds are the possible substitution products of benzoic acid are

(i) **Bromination**



(ii) **Sulphonation**



(iii) **Nitration**



NOTE

It may be noted that carboxylic acids do not undergo Friedel-Crafts reactions because

(i) the carboxyl group is strongly deactivating and

(ii) the catalyst AlCl_3 (Lewis acid) gets bonded to the carboxyl group strongly

Learning Plus

Bromination and nitration of salicylic acid

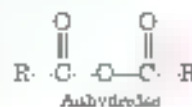
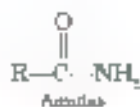
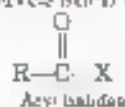
Salicylic acid contains both =CH as well as =CHOH group. On treatment with bromine water bromination of =CH and HNO_3 and H_2SO_4 nitration of =CHOH group gets knocked out resulting **decarboxylation**. Both give *o*- and *p*- products.



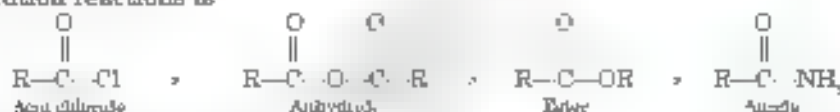
These are characteristic reactions of =CHOH group when present *o*- or *p*- to activating group such as =CH or =NH_2 .

ACID DERIVATIVES AND THEIR COMPARATIVE REACTIVITY

The =OH group of carboxylic acids can be replaced by other atoms or groups forming a number of acid derivatives such as:



The relative reactivity of different acid derivatives towards nucleophilic acyl substitution reactions is



This order of reactivity can be easily explained on the basis of relative basic strength of the leaving group. Here the leaving groups are Cl^- in acid chlorides, $\text{R}'\text{COO}^-$ in anhydrides, $\text{R}'\text{O}^-$ in esters and NH_2^- in amides. Their relative basic strength decreases as $\text{NH}_2^- > \text{R}'\text{O}^- > \text{R}'\text{COO}^- > \text{Cl}^-$.

Since a stronger base is a poor leaving group, therefore, the ease with which these leaving group leave decreases in the reverse order i.e. $\text{Cl}^- > \text{R}'\text{COO}^- > \text{R}'\text{O}^- > \text{NH}_2^-$. Thus, the relative reactivities of these acid derivatives decrease in the order acid chloride > anhydride > ester > amide.

USES OF CARBOXYLIC ACIDS

The important uses of carboxylic acids are

(a) **Uses of methanoic acid (or formic acid)**

- (i) It is used in leather tanning
- (ii) as coagulating agent for rubber latex in rubber industry
- (iii) in textile dyeing and finishing.
- (iv) as an antiseptic.
- (v) in medicine for the treatment of gout.

Competition Plus

Acid derivatives are compounds obtained by replacement of =OH group of carboxylic acids by other atoms or groups of atoms. For detail refer Competition File Page 133.

* It is used in the manufacture of rayon and in plastics, rubber and silk industries.

(ii) as vinegar in cooking and in food industry.

(2) Benzoic acid and some of its salts are used as urinary antiseptics.

(ii) Sodium salts of benzoic acid is used as a food preservative.

42) Its esters are used in perfumery

(d) 1,2- and 1,4-benzene dicarboxylic acids are obtained by the oxidation of 3- and 1,4-dimethyl benzenes respectively. 1,2-benzene dicarboxylic acid (phthalic acid) is used in the manufacture of plasticizers and resins and 1,4-benzene dicarboxylic acid (terephthalic acid) is a basic raw material for polyesters.

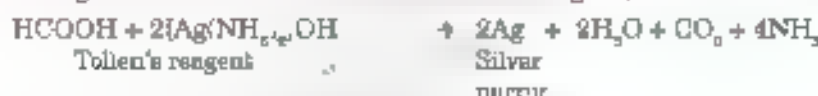
(e) Hexane-1,6-dioic acid is used in manufacture of nylon-66.

(O) Higher fatty acids are used in the manufacture of soaps and detergents.

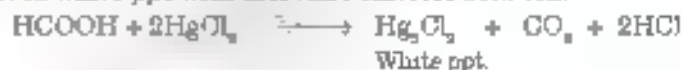
Test	Alcohols	Phenols	Carboxylic acids
1. Action on litmus	No reaction	Turn blue litmus as red	Turn blue litmus red
2. Reaction with sodium bicarbonate (NaHCO_3)	No reaction	No reaction	Give effervescence due to the evolution of CO_2
3. Reaction with sodium hydroxide (NaOH)	No reaction	Form salts	Form salts
4. Reaction with FeCl_3	No reaction	3 or characteristic colours, violet blue red, etc.	Some acids give precipitates e.g. $\text{C}_6\text{H}_5\text{COOH}$ gives buff coloured ppt.

1. Formic acid and acetic acid

Formic acid gives silver mirror test with Tollen's reagent, whereas acetic acid does not give this test.



(4.) Formic acid gives white ppt with mercuric chloride solution.



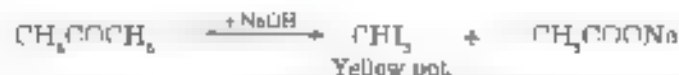
Acetic acid does not give this test

1. Acetic acid reacts with NaHCO_3 to give effervescence due to the evolution of CO_2 .



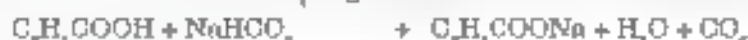
Acetone does not give effervescence with NaHCO_3 .

✓ Acetone reacts with alkaline solution of iodine & gave yellow ppt. due to the formation of Iodoform. Acetic acid does not give this test.



Acetic acid gives orange coloured ppt with 2,4-Dinitrophenyl hydrazine while acetic acid does not.

Benzoin acid reacts with NaHCO_3 to give effervescence due to the evolution of CO_2 .

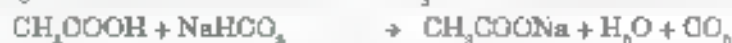


Phenol does not give effervescence.

* Phenol gives violet colour with FeCl_3 solution but benzoic acid does not give such colour

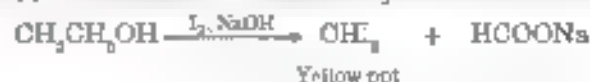
4. Ethanol and acetic acid

1. Acetic acid gives efferevescence with NaHCO_3 due to the liberation of CO_2



Ethanol does not give efferevescence with NaHCO_3

2. Ethanol gives yellow ppt with alkaline solution of I_2 while acetic acid does not give this test



Practice Problems

39. How will you prepare

- (i) ethyl bromide from propionic acid (ii) ethyl propanoate from propionic acid
(iii) acetone from acetic acid (iv) *m*-nitrobenzoic acid from benzoic acid
(v) chloroacetic acid from methyl chloride

40. Which bond C—OH or CO—H of carboxylic acids is broken when

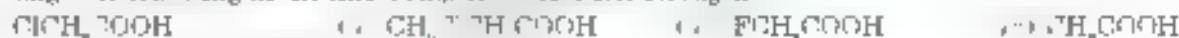
- (a) acid chloride is formed (b) acid reacts with zinc
(c) acid reacts with NH_3 to form amide.

• Ans. a C—OH b CO—H (c) CO—H

41. Which of the following is a stronger acid in each of the following pairs?

- (i) CH_3ClCOOH , CH_3FCOOH (ii) $\text{CH}_3\text{CH}_2\text{CH}_2\text{COOH}$, $\text{CH}_3\text{CH}_2\text{ClCH}_2\text{COOH}$
(iii) CH_3COOH , $\text{C}_6\text{H}_5\text{CH}_2\text{COOH}$ (iv) *m*- $\text{NO}_2\text{C}_6\text{H}_4\text{COOH}$, *p*- $\text{NO}_2\text{C}_6\text{H}_4\text{COOH}$
(v) *p*- $\text{NO}_2\text{C}_6\text{H}_4\text{COOH}$, $\text{C}_6\text{H}_5\text{COOH}$ (vi) *m*- $\text{OHC}_6\text{H}_4\text{COOH}$, *p*- $\text{OHC}_6\text{H}_4\text{COOH}$
• Ans. (i) CH_3FCOOH (ii) $\text{CH}_3\text{CH}_2\text{ClCH}_2\text{COOH}$
(iii) $\text{C}_6\text{H}_5\text{CH}_2\text{COOH}$ (iv) *p*- $\text{NO}_2\text{C}_6\text{H}_4\text{COOH}$
(v) *p*- $\text{NO}_2\text{C}_6\text{H}_4\text{COOH}$ (vi) *m*- $\text{OHC}_6\text{H}_4\text{COOH}$

42. Arrange the following in the increasing order of acidic strength

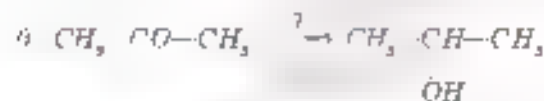


• Ans. (iii) < (iv) < (ii) < (i)

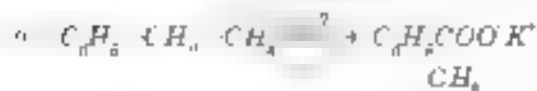
SOLVED EXAMPLES

□ Example 19

Name the reagents in the following reactions.



(D.S.B. 2015)



(D.S.B. 2015)



(A.I.S.B. 2015)



(A.I.S.B. 2015)

Solution: (i) Lithium aluminium hydride, LiAlH_4

(ii) Alkaline potassium permanganate, KMnO_4 , KOH

(iii) CH_3MgBr , H_3O^+

(iv) Cl_2 , P (Hell Volhard Zehmsky reaction)

Example 20

Predict the products of the following reactions



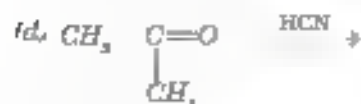
(D.S.B. 2015)



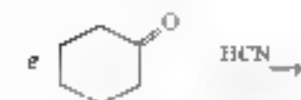
(D.S.B. 2015)



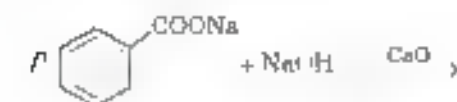
(A.I.S.B. 2015)



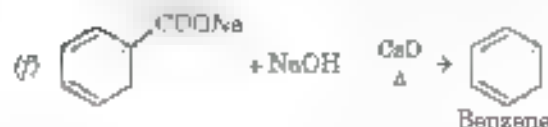
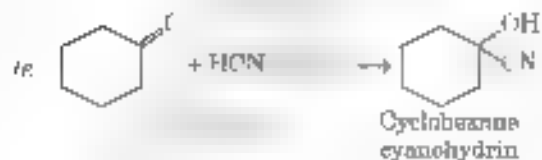
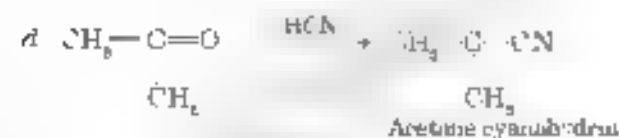
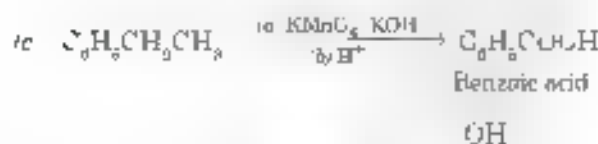
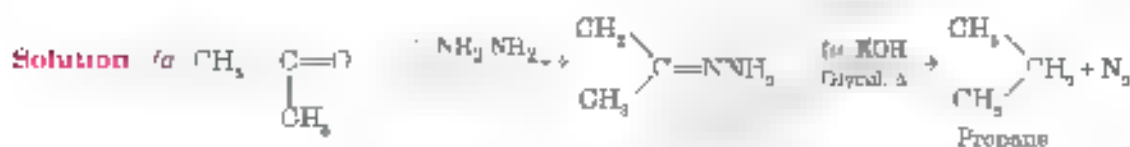
(A.I.S.B. 2015)



(A.I.S.B. 2017)



(A.I.S.B. 2017)



Example 21

(a) Discuss the reactions for the preparation of benzoic acid

(i) from ethyl benzene

(ii) using Grignard reagent

(b) How is benzoic acid converted into

(i) benzyl chloride

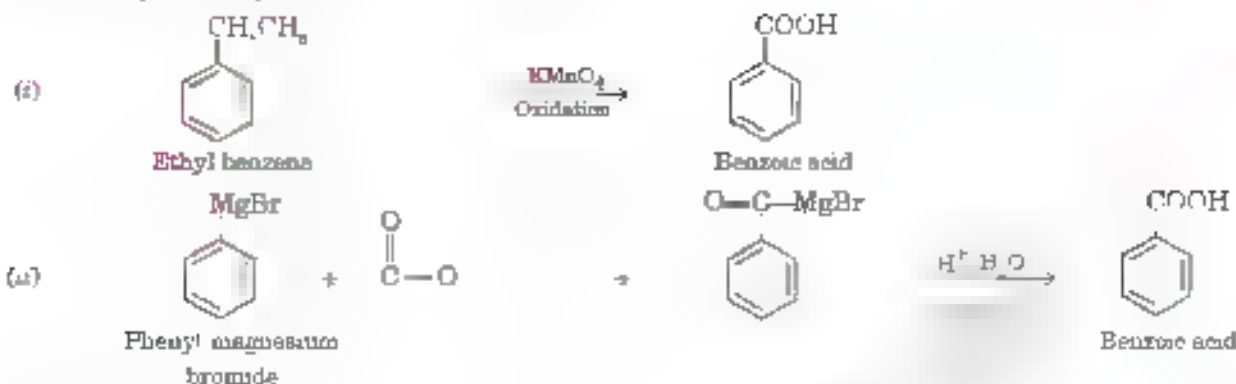
(ii) benzyl alcohol

(iii) meta nitrobenzoic acid

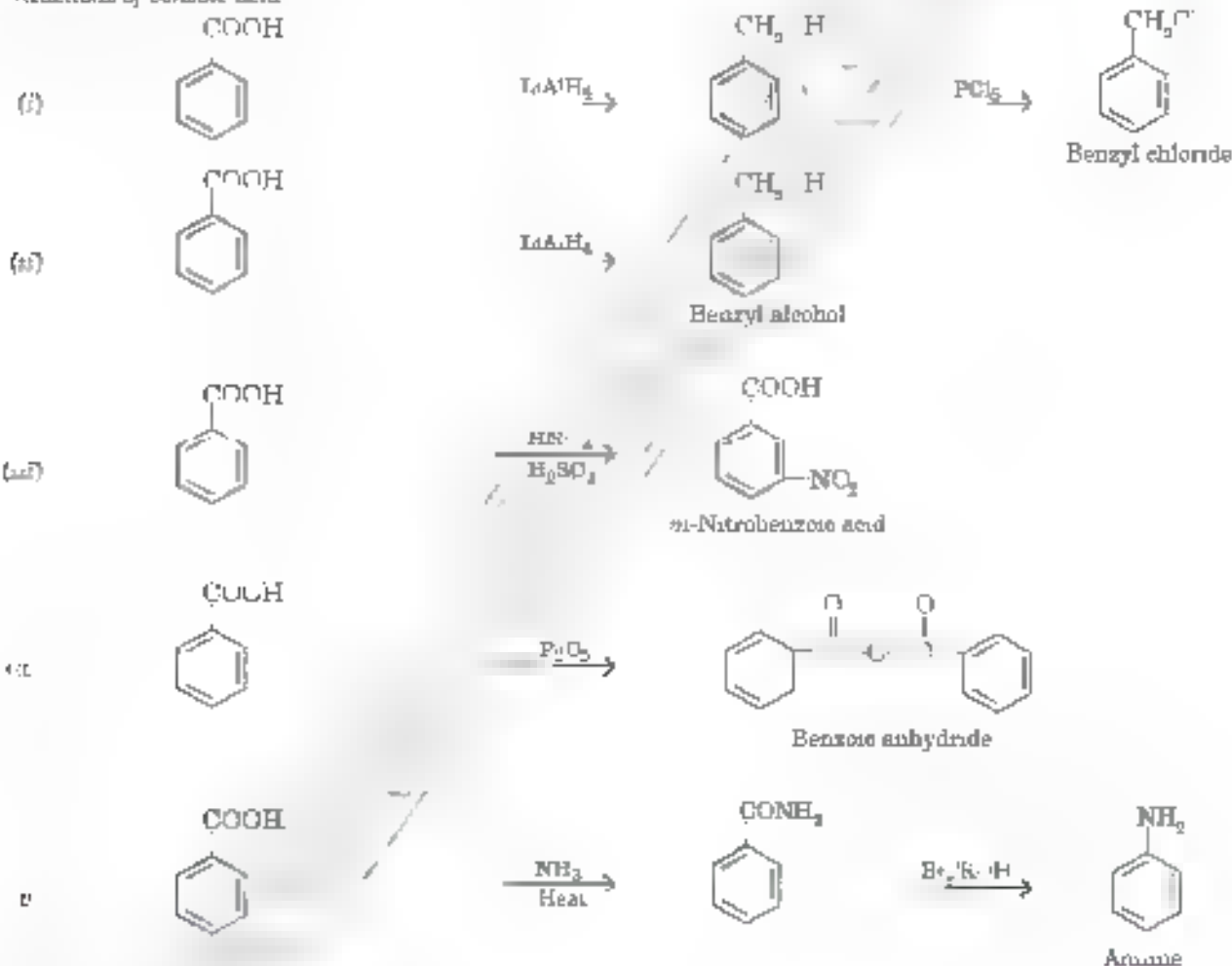
(iv) benzoic anhydride

(v) aniline

Solution (a, Preparation of benzoic acid)

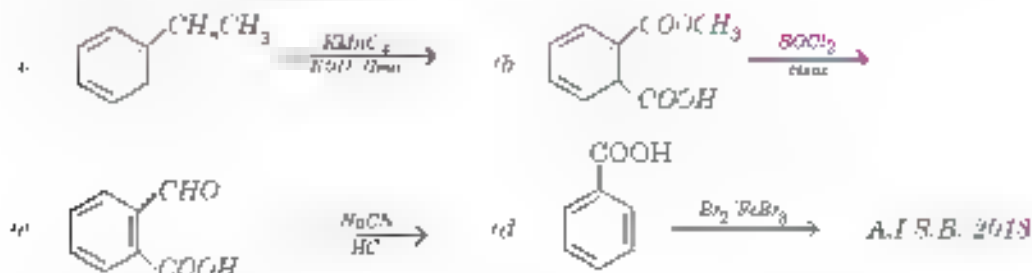


b. Reactions of benzoic acid

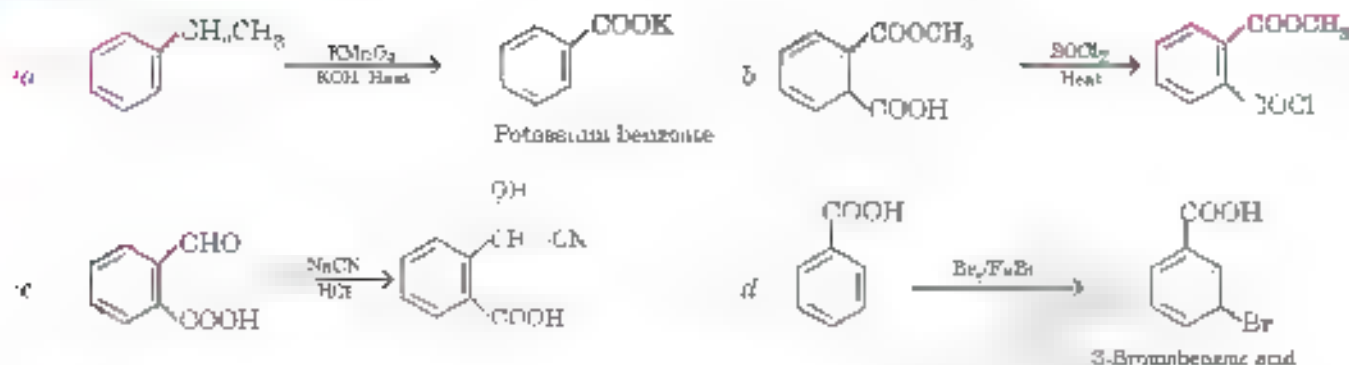


□ **Example 22**

Predict the organic products of the following reactions



Solution



□ Example 23

Describe how the following conversions are carried out:

i. Toluene to benzoic acid

A.I.S.B. 2013

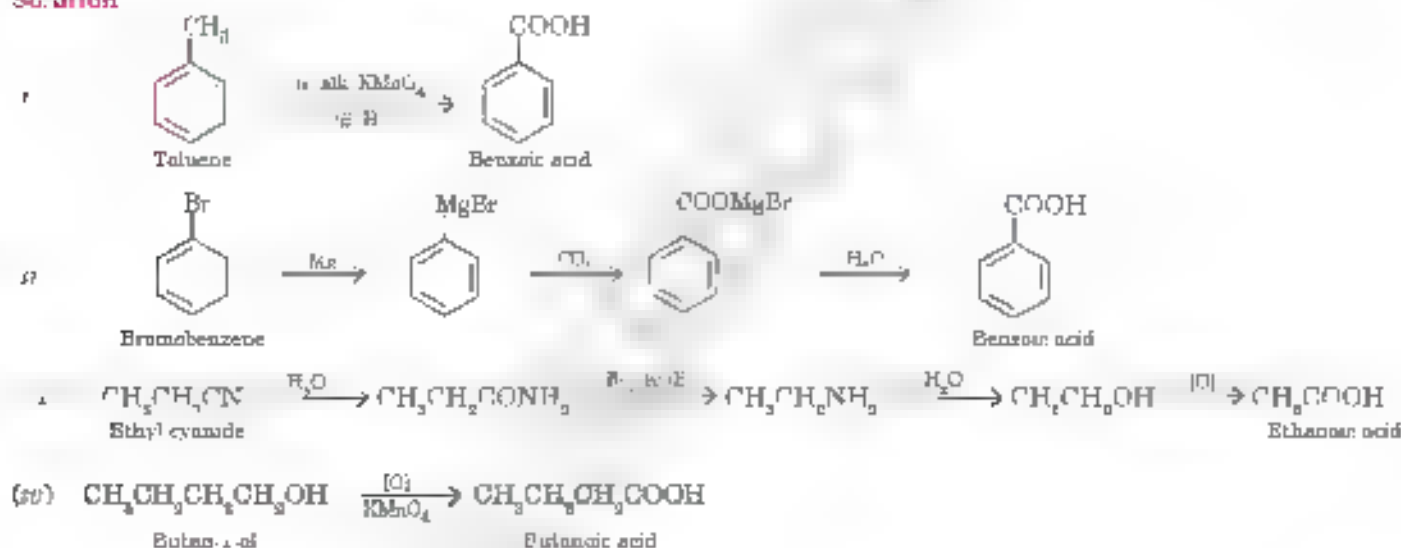
ii. Bromobenzene to benzoic acid

iii. Ethyl cyanide to ethanoic acid

iv. Butan-1-ol to butanoic acid

L.S.B. 2010

Solution



□ Example 24

How will you convert acetic acid to

malonic acid

tert-butyl alcohol

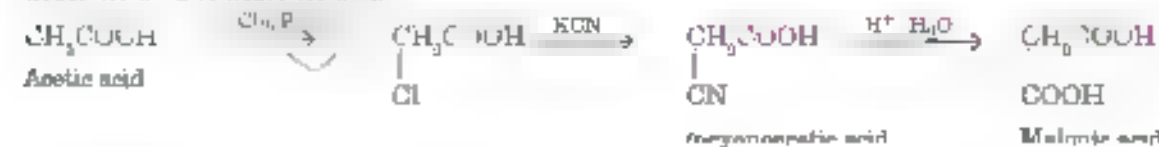
glyoxal

1,4-cyclohexadiene

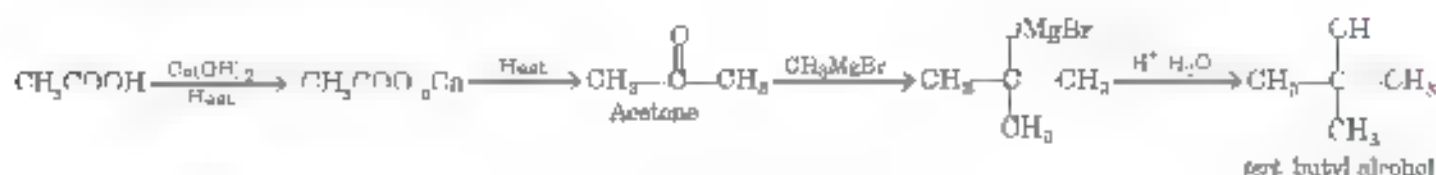
ethylmagnesium chloride

Solution

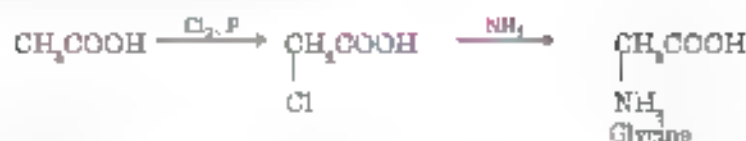
i) Acetic acid to malonic acid



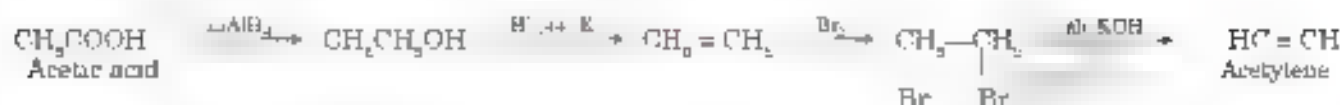
ii. Acetic acid to tert-butyl alcohol



(ii) Acetic acid to glycine



(iii) Acetic acid to acetylene



(iv) Acetic acid to ethylamine



Example 25

How will you make the following conversions?

(i) Propionic acid to acetic acid

(ii) Propionic acid to lactic acid

(iii) Ethanoic acid to propanoic acid

(iv) Propionic acid to isopropyl alcohol

(v) Acetic acid to ethanol

Megharupa S.B. 2018

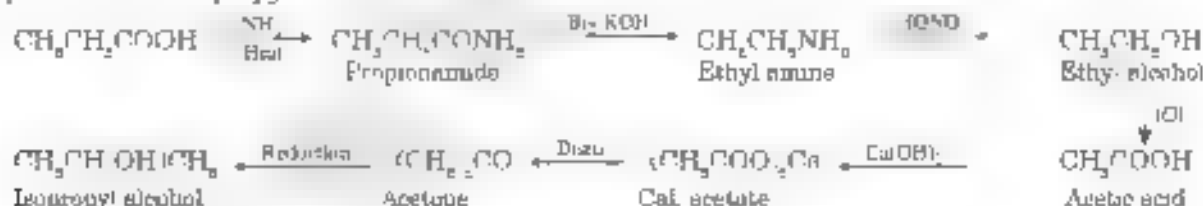
(vi) Ethene to succinic acid

Solution

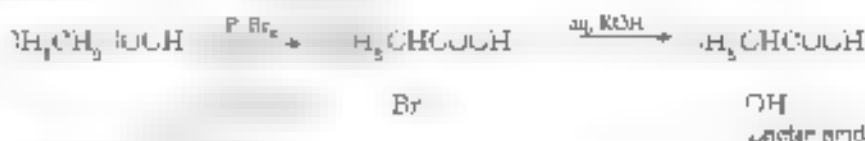
(i) Propionic acid to acetic acid



(ii) Propionic acid to isopropyl alcohol



(iii) Ethanoic acid to propanoic acid



(iv) Acetic acid to ethanol



(v) Ethanoic acid to propanoic acid

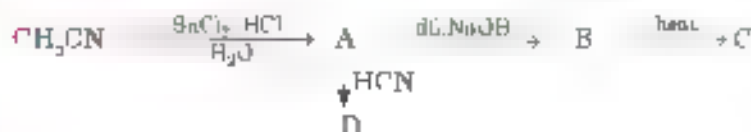


(vi) Ethene to succinic acid



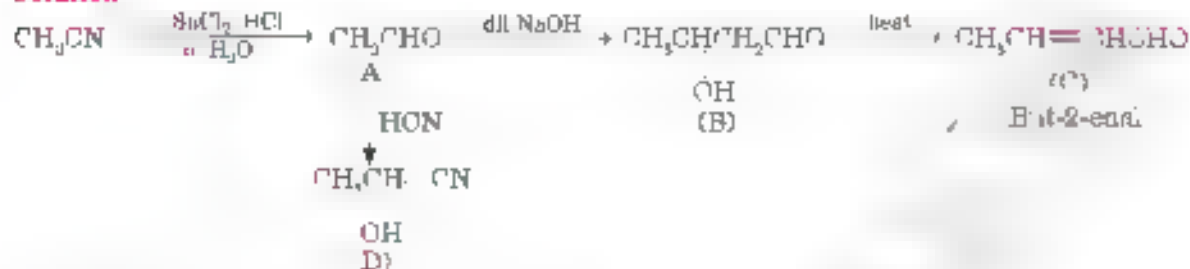
□ Example 26

Write the structures of A, B, C and D in the following reaction.



(A.I.S.B. 2018)

Solution



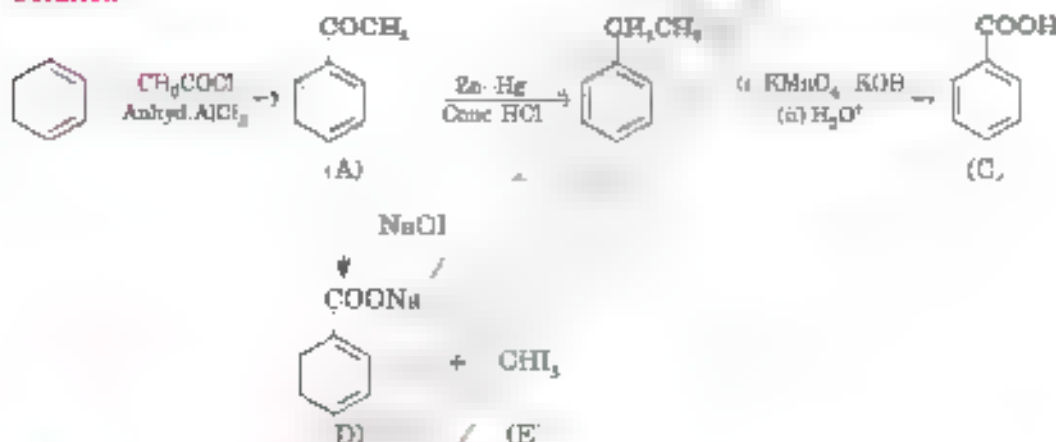
□ Example 27

Write the structures of A, B, C, D and E in the following reactions.



(I.S.B. 2018)

Solution



add on

Conceptual Questions = 2 =

Q.1 Aromatic carboxylic acids do not undergo Friedel Crafts reaction. Explain. (A.I.S.B. 2018)

Ans. Aromatic carboxylic acids do not undergo Friedel Crafts reaction because $-\text{COOH}$ group is deactivating and the catalyst aluminum chloride (Lewis acid) gets bonded to the carboxyl group.

Q.2 pK_a value of 4-nitrobenzoic acid is lower than that of benzoic acid. Explain.

(A.I.S.B. 2018)

Ans. Due to the presence of strong electron withdrawing $-\text{NO}_2$ group in 4-nitrobenzoic acid, it stabilises the carboxylate anion and hence strengthens the acid. Therefore, 4-nitrobenzoic acid is more acidic than benzoic acid and its pK_a value is lower.

Q.3 Write the IUPAC name of



(Hr. S.B. 2018)

Ans. (i) Ethanedioic acid (ii) Propanedioic acid

Q.4. Why are the boiling points of carboxylic acids higher than the corresponding alcohols?

Ans. Carboxylic acids have higher boiling points than alcohols of comparable molecular masses. For example, the boiling point of ethanoic acid is 391 K whereas that of propan-1-ol is 371 K. Both have molecular mass = 60. The higher boiling point of carboxylic acid as compared to alcohol is due to greater hydrogen bonding in acids than in alcohols. As a result, the molecules of carboxylic acids are held together by two hydrogen bonds and have more attractive forces and therefore, have higher boiling points.

Q.5. Carboxylic acids do not give the characteristic reactions of carbonyl group. Justify.

(Pb. S.B. 2018, 2015)

Ans. Carboxylic acids do not give the characteristic reactions of carbonyl group $C=O$ as given by aldehydes and ketones. In carboxylic acids, the carbonyl group is involved in resonance, as follows:



Therefore, it is not a free group. But no resonance is possible in aldehydes and ketones. They give the characteristic reactions of the group.

Q.6. Formic acid reduces Tollen's reagent. Explain.

Ans. Formic acid has aldehydic group, $\text{H}-\overset{\text{O}}{\parallel}\text{C}-\text{OH}$ and, therefore, is readily oxidised. Thus, it reduces Tollen's reagent.

Q.7. $\text{Me}_3\text{CCH}_2\text{COOH}$ is more acidic than $\text{Me}_3\text{SiCH}_2\text{COOH}$.

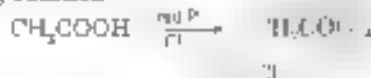
Ans. Silicon is electropositive than carbon and therefore has more electron donating effect.



As a result, the anion $\text{Me}_3\text{SiCH}_2\text{COO}^-$ conjugate base becomes less stable than $\text{Me}_3\text{CCH}_2\text{COO}^-$. Thus, $\text{Me}_3\text{CCH}_2\text{COOH}$ is more acidic than $\text{Me}_3\text{SiCH}_2\text{COOH}$.

Q.8. Acetic acid can be halogenated in the presence of red P and Cl_2 but formic acid cannot be halogenated in the same way.

Ans. Acetic acid is halogenated in the presence of red P in which substitution occurs at α -carbon atom. This is known as Hell-Volhard-Zelinsky reaction.



However, formic acid HCOOH has no α -hydrogen atom and therefore, cannot undergo HVZ reaction.

Q.9. Arrange the following in the decreasing order of acidic strength.

(a) H_2O , CH_3OH , $\text{C}_6\text{H}_5\text{OH}$, CH_3COOH

(H.P.S.B. 2018)

(b) $\text{CH}_3\text{CH}_2\text{COOH}$, HOCH_2COOH , $\text{C}_6\text{H}_5\text{CH}_2\text{COOH}$, ClCH_2COOH

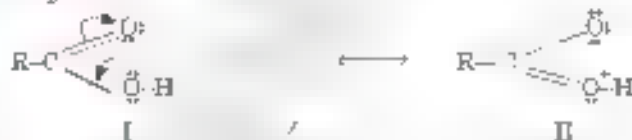
(H.P.S.B. 2016)

Ans. (a) $\text{H}_2\text{O} > \text{H}_2\text{O} > \text{H}_2\text{O} > \text{CH}_3\text{OH} > \text{C}_6\text{H}_5\text{OH} > \text{CH}_3\text{COOH}$

Q.10. Why is the bond length of $C=O$ in carboxylic acids slightly larger than that in aldehydes and ketones?

(H.P.S.B. 2016)

Ans. Carboxylic acid has resonance structures



Because of resonance structure II, there is some single bond character in $C-O$ bond, thereby making it longer than in carbonyl compounds, aldehydes and ketones.

Q.11. What is glacial acetic acid? Why is it so named?

(H.P.S.B. 2019)

Ans. 100% acetic acid which is free from water is called glacial acetic acid. The melting point of pure anhydrous acetic acid is 17°C . It is solid below this temperature and looks like 'ice' i.e., glacial.

Q.12. Complete the following:



(H.P.S.B. 2013)



Q.13. Arrange the following compounds in the increasing order of their acid strength.

(a) $\text{CH}_3\text{CH}_2\text{CH}(\text{Br})\text{COOH}$, (b) $\text{CH}_3\text{CH}(\text{Br})\text{CH}_2\text{COOH}$, (c) $(\text{CH}_3)_2\text{CHCOOH}$, (d) $\text{CH}_3\text{CH}_2\text{CH}_2\text{COOH}$

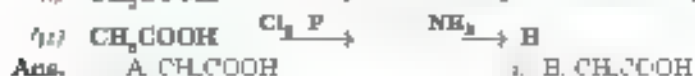
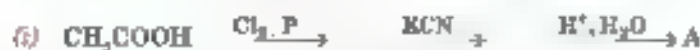
- c) Benzoic acid (b) p-nitrobenzoic acid (c) 3,4-Dinitrobenzoic acid (d) 4-Methoxybenzoic acid
(D.S.B. 2008, CBSE Sample Paper 2011)

Ans. (i) Increasing order of acid strength



- (ii) 4-Methoxy benzoic acid < a) Benzoic acid < (b) 4-Nitrobenzoic acid < (c) 3,4-Dinitrobenzoic acid

Q.14. Name A and B in the following reactions:



Ans. A. CH_3COOH

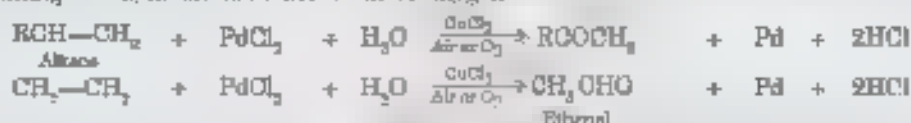
B. CH_3COOH

COOH
Malonic acid

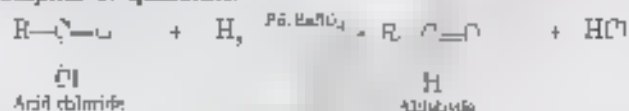
NH_2
Glycine

Key Terms & Name Reactions

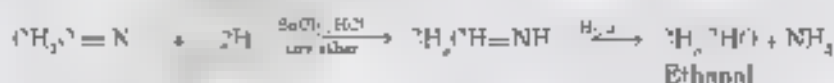
- **Carbonyl compounds** The compounds containing carbonyl group $\text{C}=\text{O}$ such as aldehydes and ketones are called carbonyl compounds.
- **α -hydrogen** The hydrogen attached to the carbon atom next to carbonyl group i.e. -CHO , -C(=O)-COOH
- **Wacker process** Alkenes can be converted into aldehydes and ketones by treating with acidified aqueous solution of PdCl_2 containing CuCl_2 in the presence of air or oxygen.



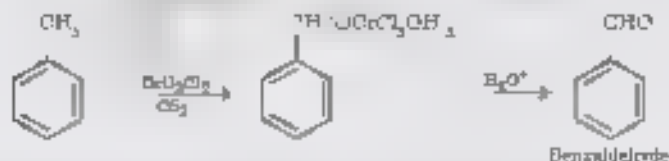
- **Rosenmund's reduction** Acid chlorides are converted into aldehydes by catalytic hydrogenation in the presence of palladium (Pd) catalyst supported over barium sulphate. The catalyst mixture is poisoned by the addition of a small amount of sulphur or quinoline.



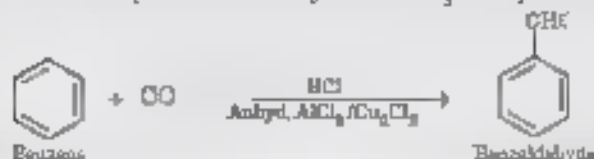
- **Stephen reduction** Alkyl cyanides or nitriles when reduced with stannous chloride and hydrochloric acid or absolute ether followed by hydrolysis give aldehydes.



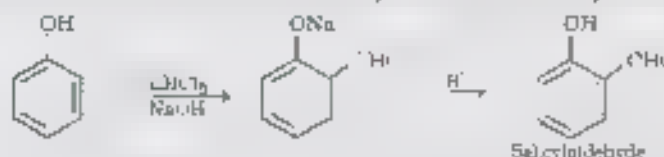
- **Etard's reaction** Alkyl benzenes can be oxidised to benzaldehyde with chromyl chloride CrO_2Cl_2 in CCl_4 or CS_2 .



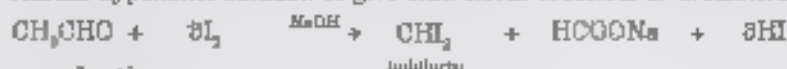
- **Gattermann Koch aldehyde synthesis** Benzaldehyde is prepared by treating a mixture of CO + HCl with benzene at 323 K in the presence of anhydrous AlCl_3 or cuprous chloride catalyst.



- **Rasmer Tiemann reaction:** Phenolic aldehydes are obtained by treating phenol with CHCl_3 in aqueous NaOH



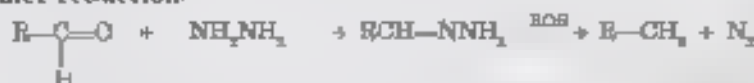
- **Haloform reaction:** Aldehydes and ketones having at least one methyl group linked to the carbonyl carbon are easily oxidised by sodium hypohalite solution to give chloroform, iodoform or bromoform



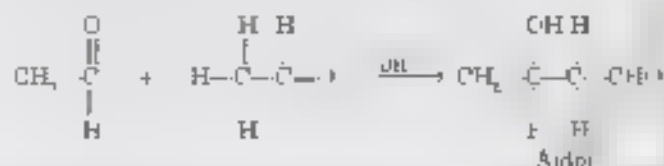
- **Clemmensen reduction:**



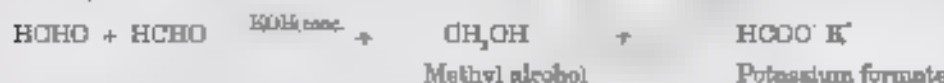
- **Wolff-Kishner reduction:**



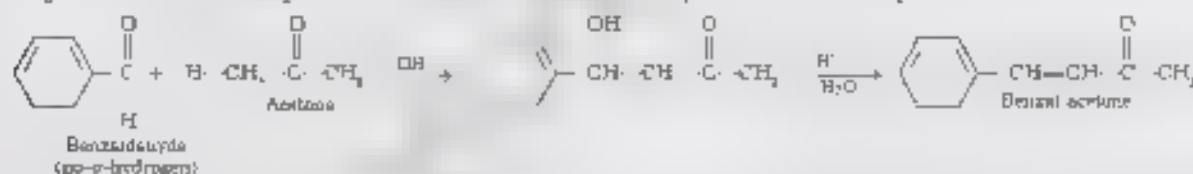
- **Aldol condensation:** Aldehydes and ketones contain *or* at least one α -hydrogen (H atom attached to the C atom adjacent to the carbonyl group) undergo self condensation in the presence of dilute alkali to form β -hydroxy α -aldehyde aldol or β -hydroxy ketone ketol respectively



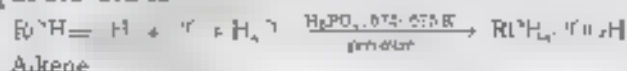
- **Cannizzaro's reaction:** Aldehydes which do not contain any α -hydrogen atom such as formaldehyde (HCHO) and benzaldehyde ($\text{C}_6\text{H}_5\text{CHO}$) undergo self oxidation and reduction reaction on treatment with concentrated alkali. In this reaction, one molecule is oxidised to acid while another is reduced to alcohol.



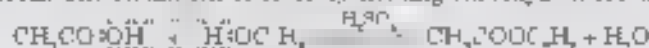
- **Claissen Schmidt reaction:** The reaction of condensation between an aromatic aldehyde or ketone and an aliphatic aldehyde or ketone in the presence of dilute alkali to form α, β unsaturated compound.



- **Acetylation:** The process of replacement of an active hydrogen of alcohols, phenols or amines with acetyl group to form corresponding esters or amides
- **Decarboxylation:** The process of removal of a molecule of CO_2 from a carboxylic acid
- **Koch reaction:** Carboxylic acids are obtained on a large scale by heating alkanes with CO and steam under pressure with H_3PO_4 at 573–673 K



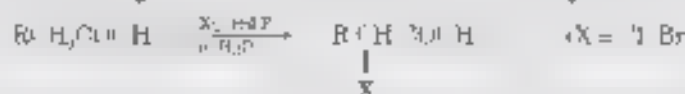
- **Esterification:** The formation of ester by heating carboxylic acids with alcohols in the presence of conc. H_2SO_4 or HCl



- **Hunsdiecker reaction:** Silver salts of carboxylic acids on treatment with Br_2 in the presence of CaCl_2 give alkyl bromides having one C atom less than the parent acid.



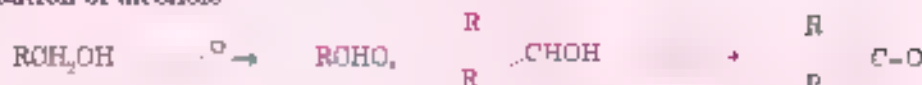
- **Hell-Volhard-Zelinsky (HVZ) reaction:** Reaction of carboxylic acids having α -hydrogen atom



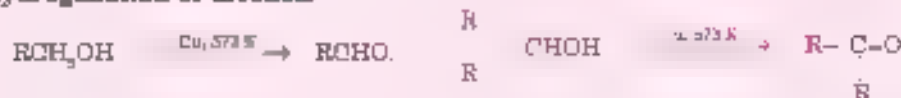
QUICK CHAPTER ROUND UP

Preparation of Aldehydes and Ketones

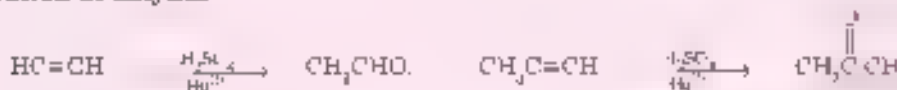
Oxidation of alcohols



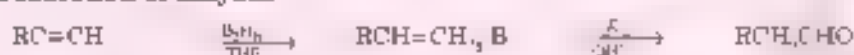
Dehydrogenation of alcohols



Hydration of alkynes



Hydroboration of alkynes



Ozonolysis of alkenes



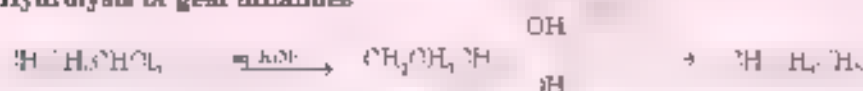
From calcium salts



Wacker Process

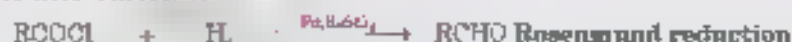


Hydrolysis of gem dihalides



Preparation of Aldehydes only

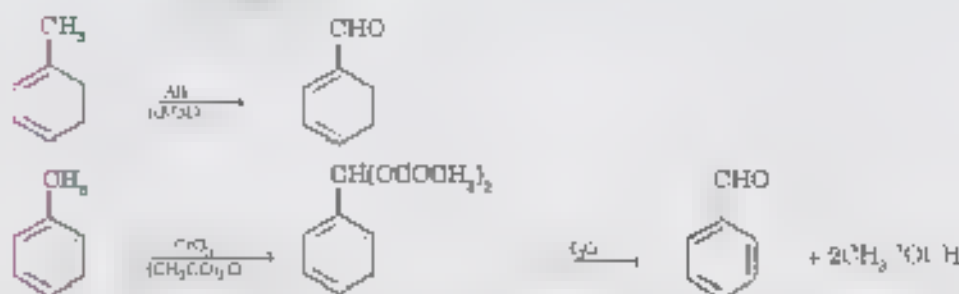
- Reduction of acid chlorides

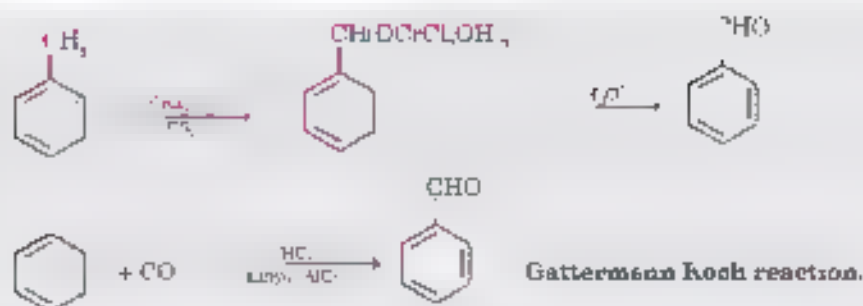


- Reduction of alkyl cyanides



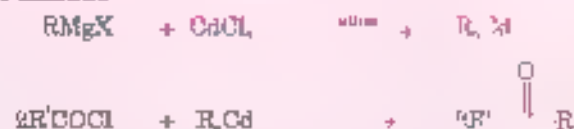
- From aromatic hydrocarbon



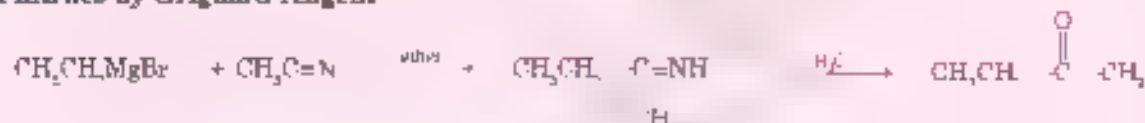


Preparation of Ketones only

- From acyl halides



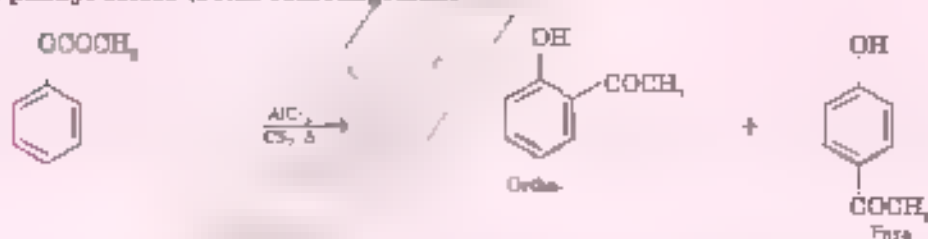
- From nitriles by Grignard reagent



- From benzene or substituted benzene

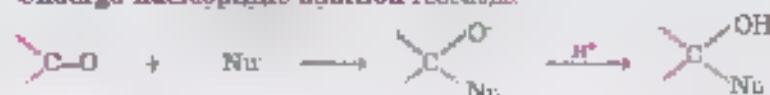


- From phenyl esters (Fries rearrangement)

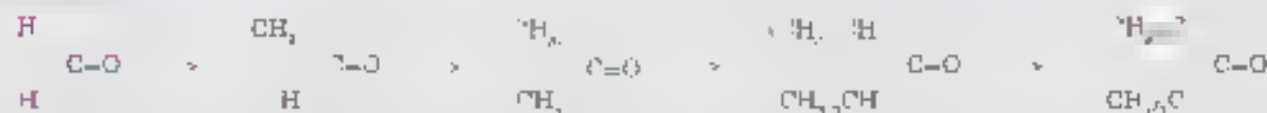


Reactions of Aldehydes and Ketones

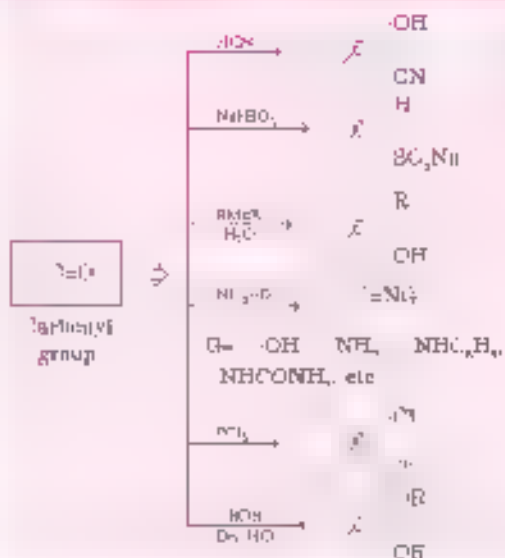
- Undergo nucleophilic addition reactions.



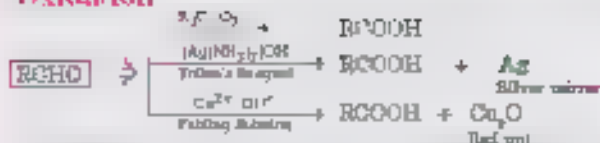
Reaction IV



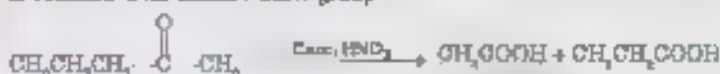
Addition Reactions of Carbonyl Group



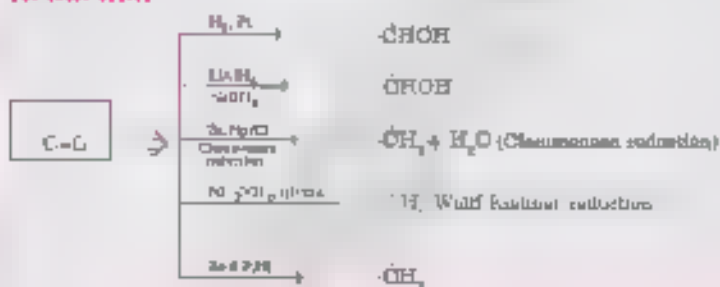
Oxidation



Retention in **drinker** conditions are subjected to **drinker** bonds with rupture of bond between carbonyl C and α -C. In unsymmetrical ketones, carbonyl group is retained with smaller alkyl group.



Reduction



CARBOXYLIC ACIDS

Preparation of Carboxylic Acids

Oxidation of alcohols

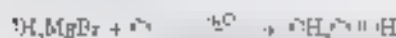


Oxidation of aldehydes and ketones

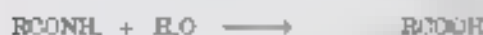
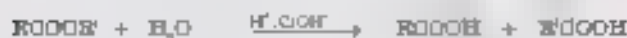
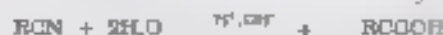


Ketone

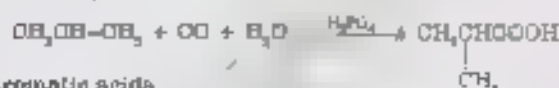
Brigant rangem



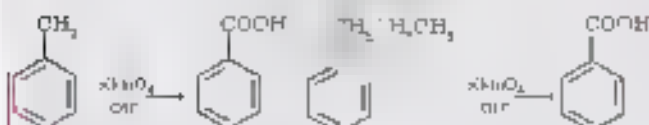
Hydrolysis



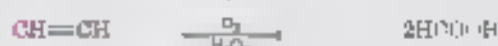
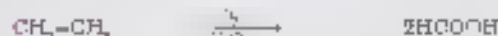
Carboxylation of alkenes



Aromatic acids



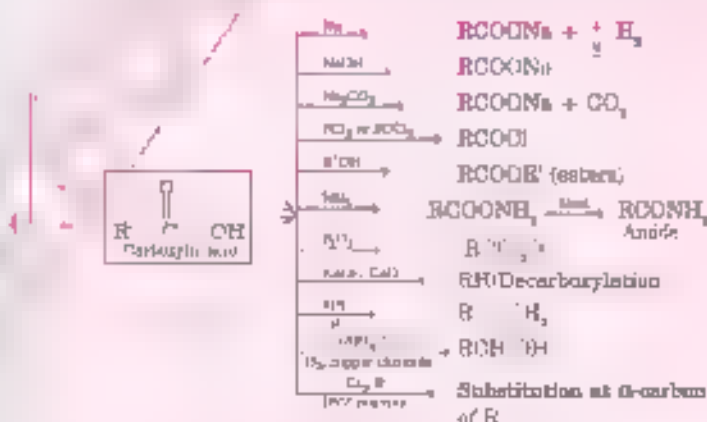
Oxidation



By passing CO on sodium alkoxide.



Reactions of Carboxylic Acids and its Derivatives.



Aromatic carboxylic acids undergo electrophilic substitution reactions in which carboxylic group acts as a deactivating and meta directing group.

They do not undergo Friedel Crafts reaction.

Effect of substituents on acidic strength of acids. In general electron withdrawing groups (EWG) increase the stability of the carboxylate ion by delocalising the negative charge and hence increase the acidity of the carboxylic acid. Conversely electron donating groups (EDG) decrease the stability of the carboxylate ion by concentrating the negative charge and hence decrease the acidity of the carboxylic acid.

The electron releasing groups like $-\text{CH}_3$, $-\text{OH}$, $-\text{OCH}_3$ and $-\text{NH}_2$ make benzoic acid weaker while electron withdrawing groups like $-\text{Cl}$, $-\text{NO}_2$ etc., make benzoic acid stronger.

The acid having highest electron withdrawing group is the strongest acid among the three isomers due to effect known as ortho effect.

Among *p*- and *m*-isomers, *p*-isomer has more acidic character than *m*-isomer for electron withdrawing group. On the other hand, for electron releasing group like $-\text{OH}$ group, *m*-isomer is stronger acid than benzoic acid while *p*-isomer is weaker than benzoic acid.

Phenols are less acidic (pK_a is about 10) than carboxylic acids.



NCERT FILE

Solved

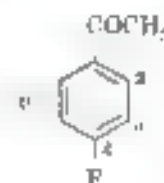
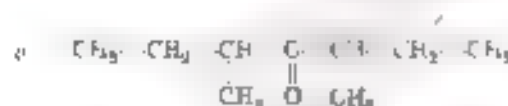
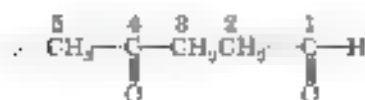
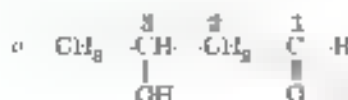
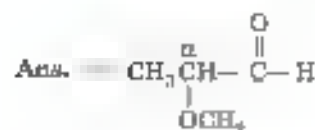


NCERT

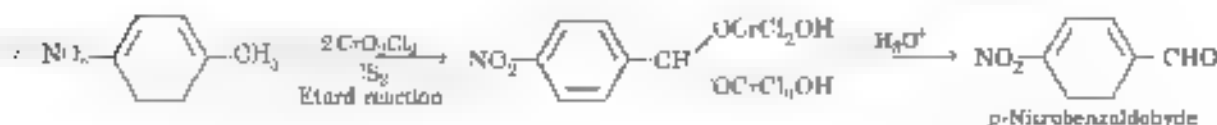
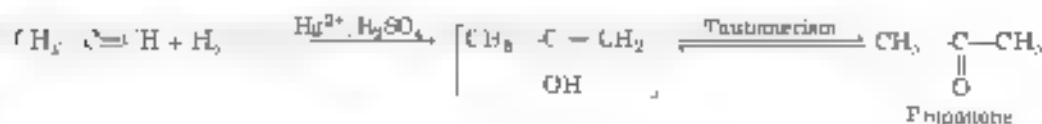
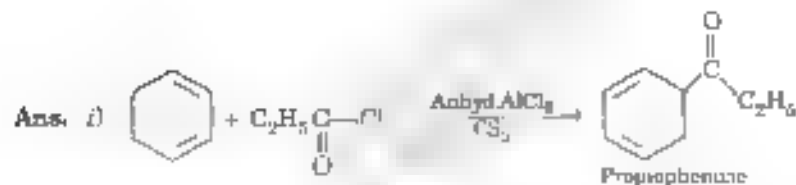
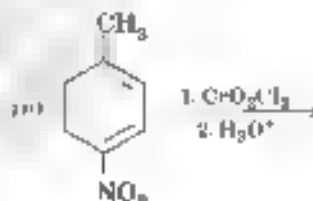
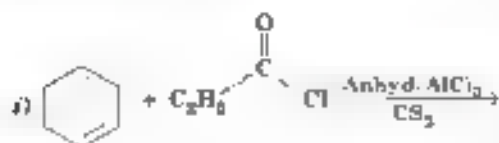
In-text Questions

Q.1. Write the structures of the following compounds

- i) α -Methoxypropionaldehyde ii) 3-Hydroxybutanal iii) 2-Hydroxycyclopentanecarbaldehyde
 (iv) 4-Oxopentanal v) Di-*sec*-butyl ketone (vi) 4-Fluorocetophenone



Q.2. Write the structures of products of the following reactions



Q.3. Arrange the following compounds in the increasing order of their boiling points



Ans. The molecular mass of all these four compounds are comparable (CH_3OH 44, $\text{CH}_3\text{CH}_2\text{OH}$ 46, CH_3OCH_3 46, $\text{CH}_3\text{CH}_2\text{CH}_3$ 44). Among these $\text{CH}_3\text{CH}_2\text{OH}$ undergoes extensive intermolecular H-bonding and it exists as associated molecule and hence its boiling point is the highest. $\text{CH}_3\text{CH}_2\text{OH}$ is more polar than CH_3OCH_3 and therefore, dipole-dipole interactions are stronger in $\text{CH}_3\text{CH}_2\text{OH}$ than in CH_3OCH_3 . Hence the boiling point of $\text{CH}_3\text{CH}_2\text{OH}$ is higher than that of CH_3OCH_3 . In $\text{CH}_3\text{CH}_2\text{CH}_3$, there are only weak van der Waals forces and hence its boiling point is the lowest. The correct order of increasing order of boiling points is

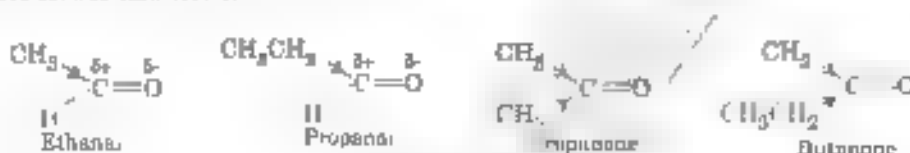


Q.4. Arrange the following compounds in increasing order of their reactivity in nucleophilic addition reactions

i) Ethanal, Propanal, Propanone, Butanone

ii) Benzaldehyde, *p*-Tolualdehyde, *p*-Nitrobenzaldehyde, Acetophenone

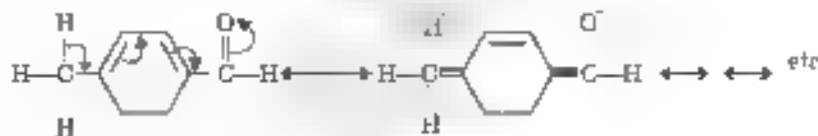
Ans. As we move from ethanal to propanal to propanone to butanone, the +I inductive effect of alkyl group increases. As a result, the +ve charge on the carbon atom of the carbonyl group progressively decreases and hence attack by nucleophile becomes slower and slower.



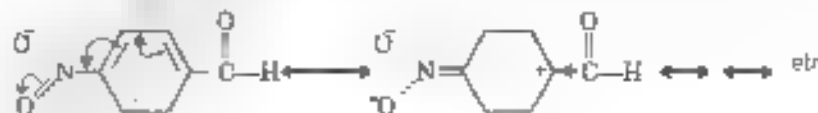
Thus, the reactivity increases in the order



Among these compounds, acetophenone is a ketone while all others are aldehydes, therefore, acetophenone is least reactive. In *p*-tolualdehyde, there is a methyl (CH_3) group at the *para* position w.r.t the carbonyl group which increases electron density or decreases +ve charge on the carbonyl group by hyperconjugation effect, thereby making it less reactive than benzaldehyde.



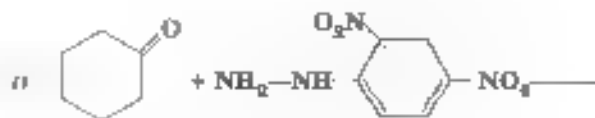
On the other hand, in *p*-nitrobenzaldehyde, the NO_2 is an electron withdrawing group. It withdraws electrons, both by inductive and resonance effect, thereby decreasing electron density or increasing +ve charge on the carbon atom of the carbonyl group. This facilitates the attack of the nucleophile and hence makes it more reactive than benzaldehyde.

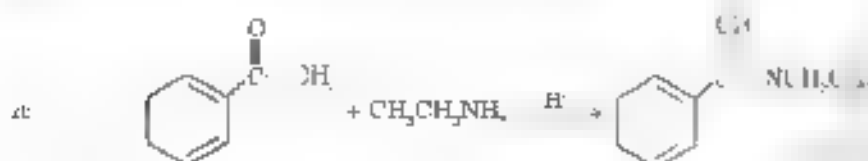
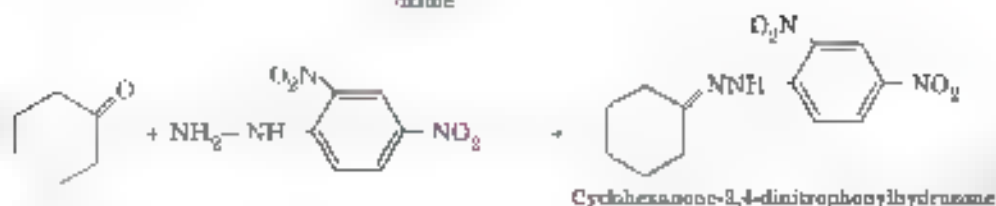


Therefore, the correct order of reactivity is

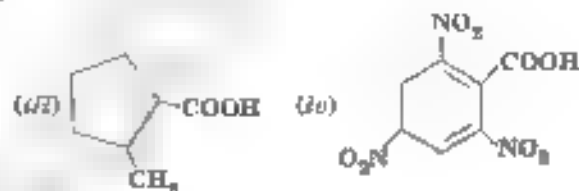
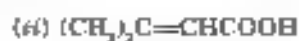


Q.5. Predict the products of the following reactions :





Q.6. Give the IUPAC names of the following compounds



Ans. (i) 3-Phenylpropanoic acid

(ii) 2-Methylbut-2-enoic acid

(iii) 3-Methylbut-2-enoic acid

(iv) 2,4,6-Trinitrobenzoic acid

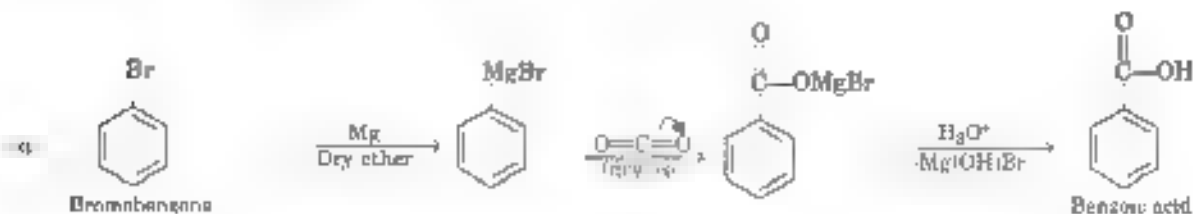
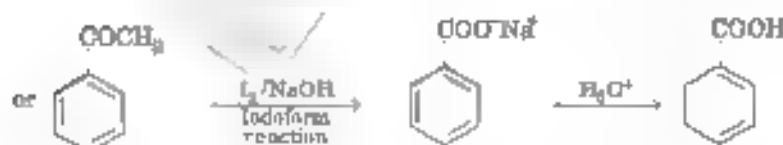
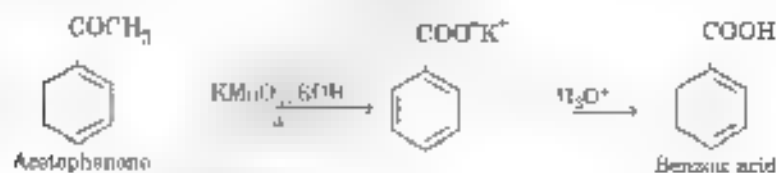
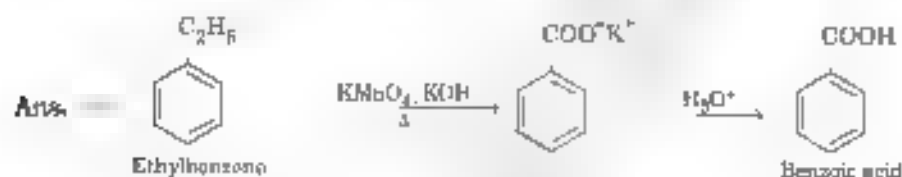
Q.7 Show how each of the following compounds could be converted to benzoic acid.

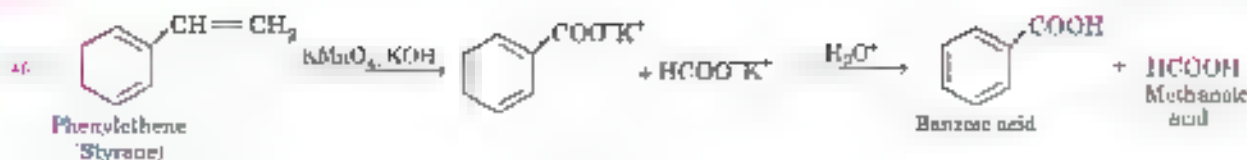
(i) Ethylbenzene

(ii) Acetophenone

(iii) Bromobenzene

(iv) Phenylethene (Styrene)





Q.5. Which acid of each pair shown here would you expect to be stronger ?



Textbook Exercises

Q.1. What is meant by the following terms ? Give an example in each case.

(i) Cyanohydrin

(ii) Semicarbazone

(iii) Hemiacetal

(iv) Ental

(v) 2,4-DNP-derivative

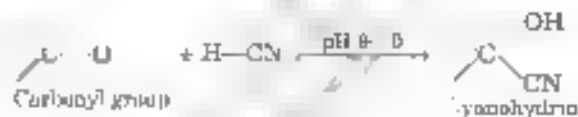
(vi) Acetal

(vii) Oxime

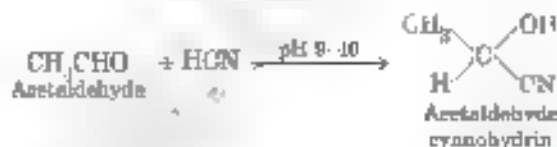
(viii) Imine

(ix) Schiff's base

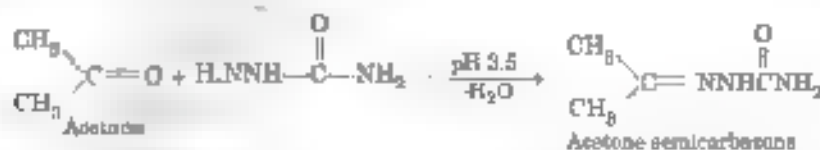
Ans. The compounds containing hydroxy- and cyano groups on the same carbon atom are called **cyanohydrins**. These are also called gem-hydroxynitriles. These are obtained by the addition of H^+CN to a carbonyl group in weakly basic medium.



e.g.,



1. **Semicarbazones** are the derivatives of aldehydes and ketones obtained by the action of semicarbazide on them in weakly acidic medium.



These are used for identification and characterization of aldehydes and ketones.

2. Gem-alkoxy alcohols are called **hemiacetals**. These are obtained by the addition of one molecule of anhydrous alcohol to an aldehyde in the presence of dry HCl gas.

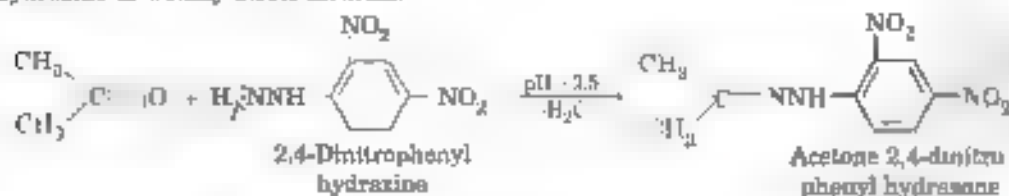


3. Gem-dialkoxy alkanes are called **ketals**. In these compounds the two alkoxy groups are present on the same carbon within the chain. These are produced by the reaction of ketone with ethylene glycol in the presence of dry HCl gas.

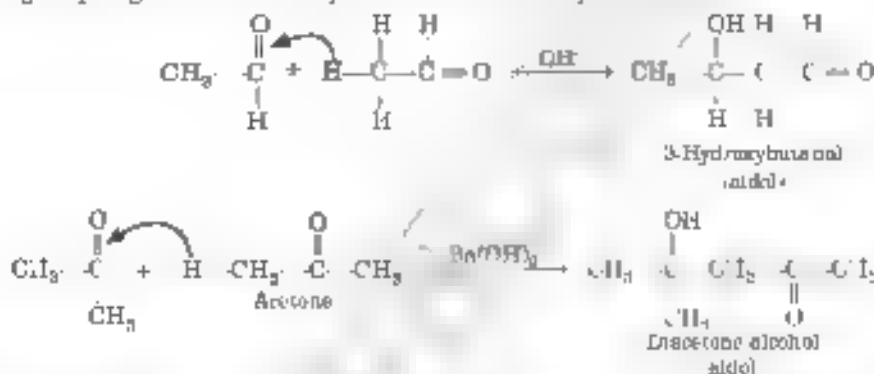


These are readily hydrolysed by dilute mineral acids to regenerate the original ketones. Therefore ketals are used for the protection of keto groups in organic synthesis.

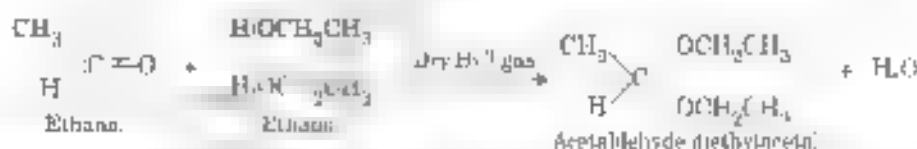
- (c) **2,4-Dinitrophenyl hydrazones** 2,4-DNP derivative are produced when aldehydes or ketones react with 2,4-dinitrophenyl hydrazine in weakly acidic medium.



- (d) **Aldols** are β -hydroxyaldehydes or ketones which are produced by the condensation of two molecules of aldehydes or ketones containing α -hydrogen atoms in the presence of a dilute aqueous alkali.



- (e) **Acetal**. These are dialkory compounds in which two alkoxy groups are present on the terminal carbon atom. These are produced by the action of an aldehyde with two equivalents of a monohydric alcohol in the presence of dry HCl gas.



- (f) **Oximes** are formed when aldehydes or ketones react with hydroxyl amines in weakly acidic medium.

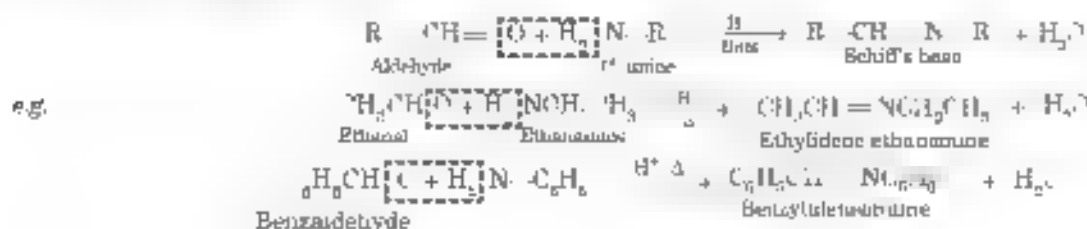


- (g) **Imines**. These are the compounds containing $-\text{CH}=\text{N}-$ group and are produced when aldehydes and ketones react with ammonia derivatives.



$\text{Z} = \text{NH}_3, \text{OH}, \text{NHC}_2\text{H}_5, \text{NHNHC(ONH}_2)_2$, etc.

- (h) **Schiff's base**. Aldehydes and ketones react with primary aliphatic or aromatic amines to form azomethines which are also called Schiff's bases.



Q.2. Name the following compounds according to IUPAC system of nomenclature



Ans. (i) 4-Methylpentanal

(ii) But-2-enal

(iii) 3,3,5-Trimethylhexan-2-one

(iv) Benzene-1,4-dicarbaldehyde



(v) 6-chloro-4-ethylhexan-3-one

(vi) Pentane-2,4-dione

(vii) 2,2-Dimethylbutanoic acid

Q.3. Draw the structures of the following compounds

(i) 3-Methylbutanal

(ii) *p*-methylbenzaldehyde

(iii) 4-Chloropentan-2-one

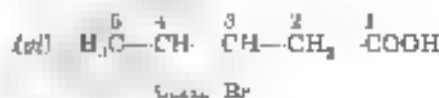
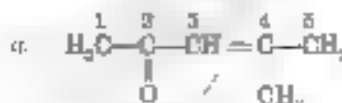
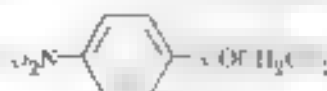
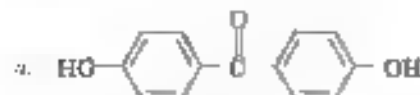
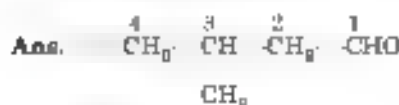
(iv) *p,p*-Dihydroxybenzophenone

(v) *p*-Nitropropioophenone

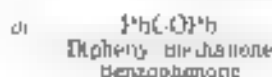
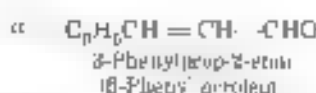
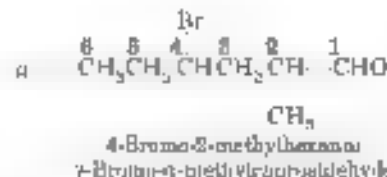
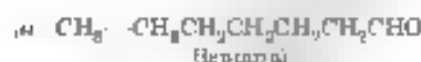
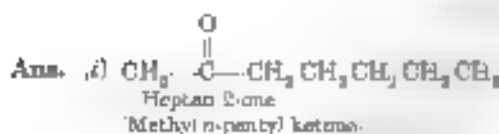
(vi) 4-Methylpent-3-en-2-one

(vii) 5-Bromo-4-phenylpentanoic acid

(viii) Hex-2-en-4-ynoic acid



Q.4. Write the IUPAC names of the following ketones and aldehydes. Wherever possible, give also common names.



Q.5. Draw structures of the following derivatives

(i) The 2,4-dinitrophenylhydrazone of benzaldehyde

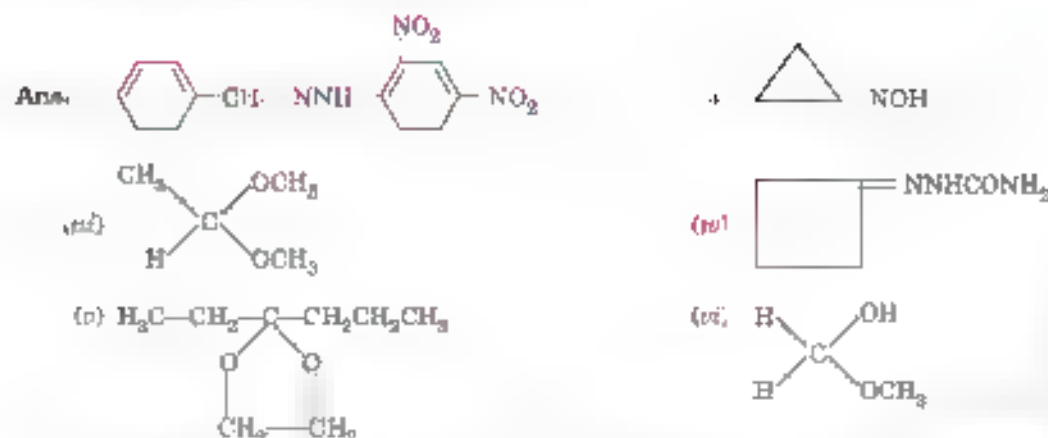
(ii) Acetaldehydimethylacetal

(iii) The ethylene ketal of hexan-3-one

(iv) Cyclopropanone oxime

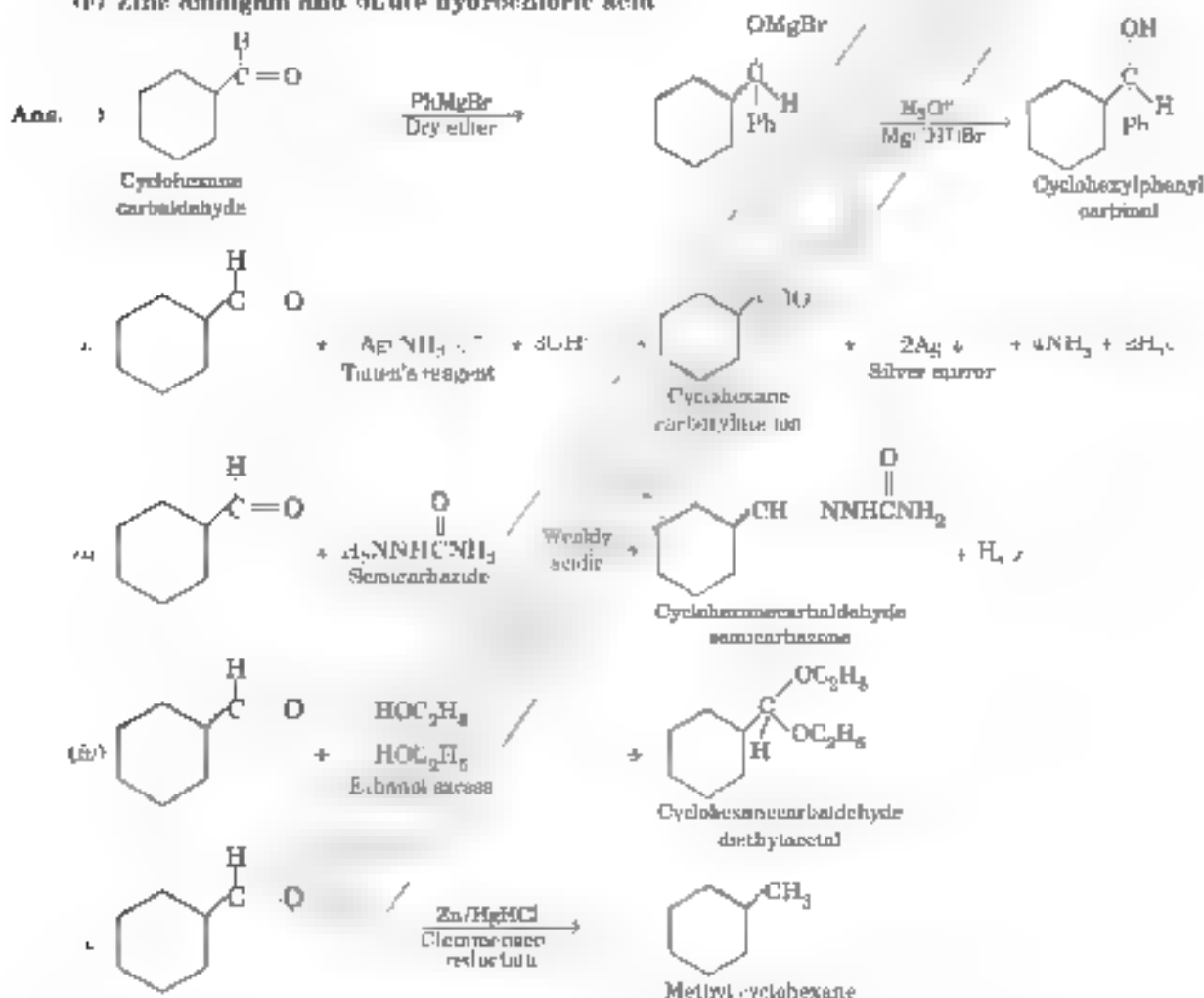
(v) The semicarbazone of cyclobutanone

(vi) The methyl hemiacetal of formaldehyde



Q.6. Predict the product formed when cyclohexanecarbaldehyde reacts with following reagents

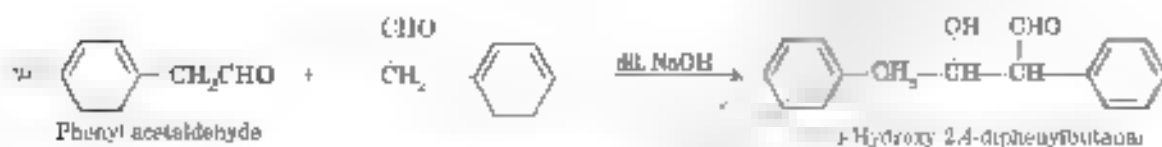
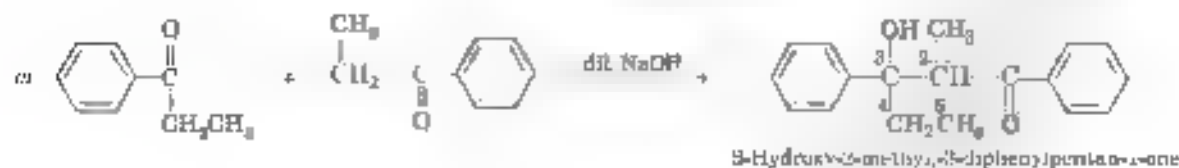
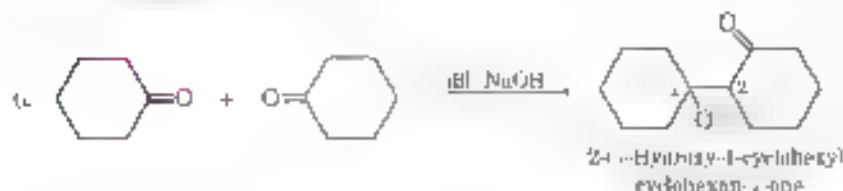
- (i) PhMgBr and then H_3O^+ (ii) Tollen's reagent
 (iii) Semicarbazide and weak acid (iv) Excess ethanol and acid
 (v) Zinc amalgam and dilute hydrochloric acid



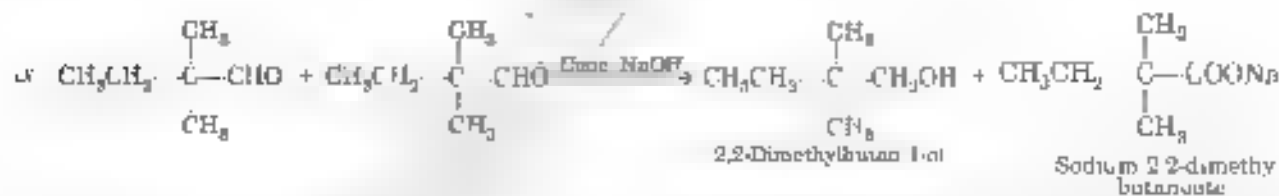
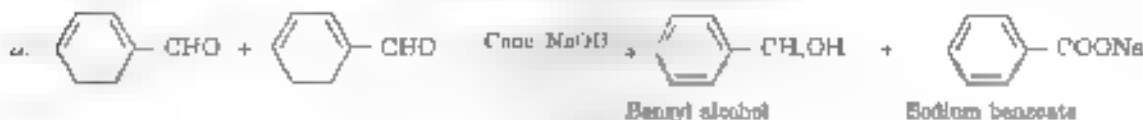
Q.7. Which of the following compounds would undergo aldol condensation, which the Cannizzaro reaction and which neither? Write the structures of the expected products of aldol condensation and Cannizzaro reaction.

- (i) Methanal (ii) 2-Methylpentanal (iii) Benzaldehyde
 (iv) Benzophenone (v) Cyclohexanone (vi) 1-Phenylpropanone
 (vii) Phenylacetaldehyde (viii) Butan-1-ol (ix) 2,2-Dimethylbutanal

Ans.



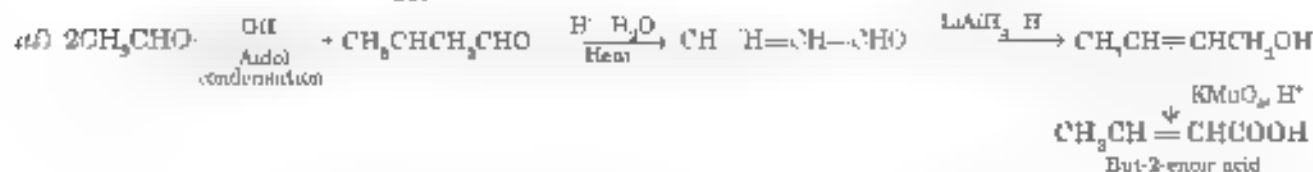
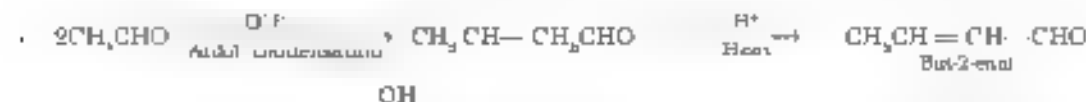
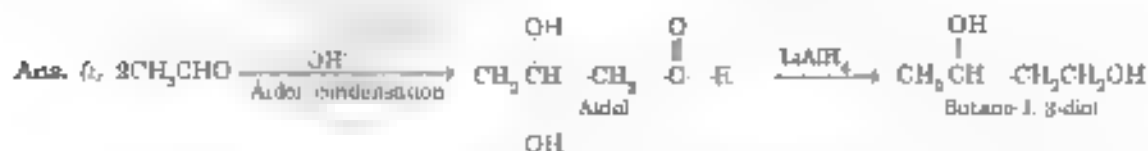
• Methanal, *m*-benzaldehyde and *m*-2,2-dimethylbutanal don't contain α -hydrogen and therefore, undergo Cannizzaro's reaction.



• Benzophenone is a ketone having no α -hydrogen and *m*-benzyl-al is an alcohol. These neither undergo aldol condensation nor Cannizzaro's reaction.

Q.8. How will you convert ethanal into the following compounds?

i) Butane-1,3-diol ii) But-2-enal iii) But-2-enoic acid



Q.9. Write structural formulas and names of the four possible aldol condensation products from propanal and butanal. In each case, indicate which aldehyde served as nucleophile and which as electrophile.

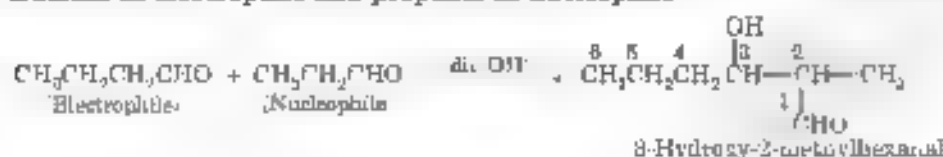
Ans. i. Propanal as electrophile as well as nucleophile



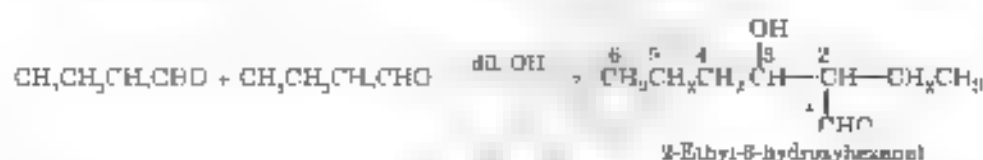
ii. Propanal as electrophile and butanal as nucleophile



iii. Butanal as electrophile and propanal as nucleophile

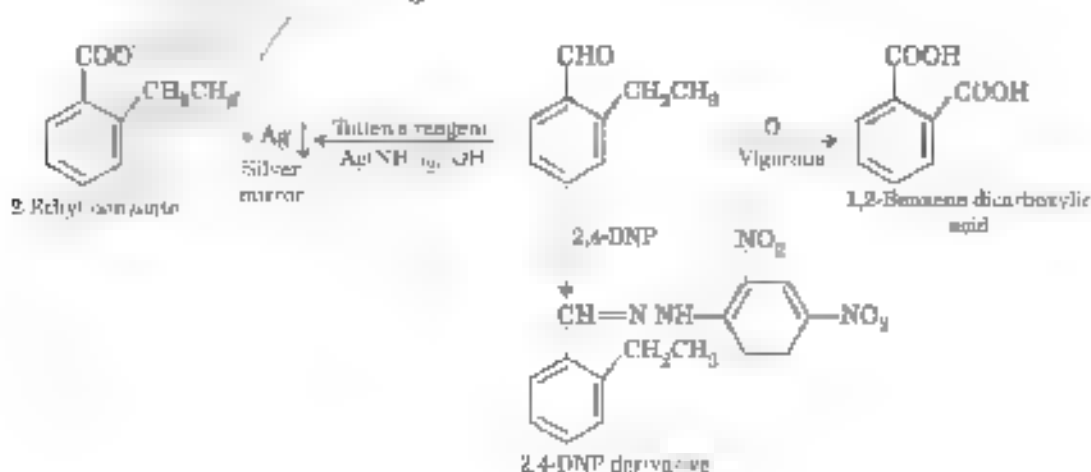
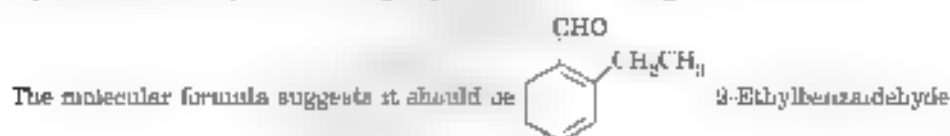


iv. Butanal as electrophile as well as nucleophile



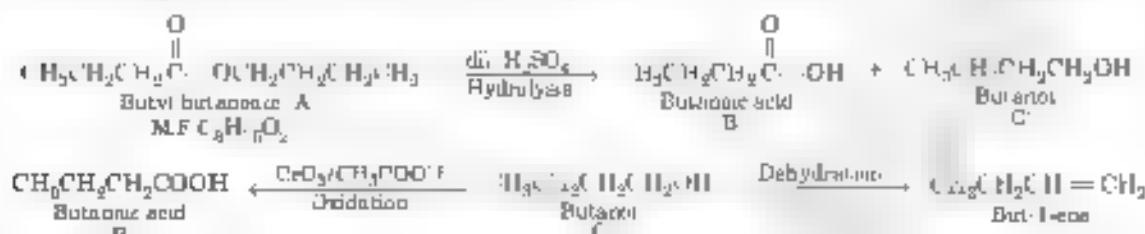
Q.10. An organic compound with the molecular formula $\text{C}_9\text{H}_{10}\text{O}$ forms 2,4-DNP derivative, reduces Tollens' reagent and undergoes Cannizzaro reaction. On vigorous oxidation, it gives 1,2-benzenedicarboxylic acid. Identify the compound.

Ans. The given compound forms 2,4-DNP derivative. Therefore, it is an aldehyde or ketone. Since it reduces Tollens' reagent, it must be an aldehyde. The compound undergoes Cannizzaro's reaction, so it does not contain α -hydrogen. On vigorous oxidation, it gives 1,2-benzenedicarboxylic acid, it means that it must be containing alkyl group at 2-position with respect to CHO group on the benzene ring.



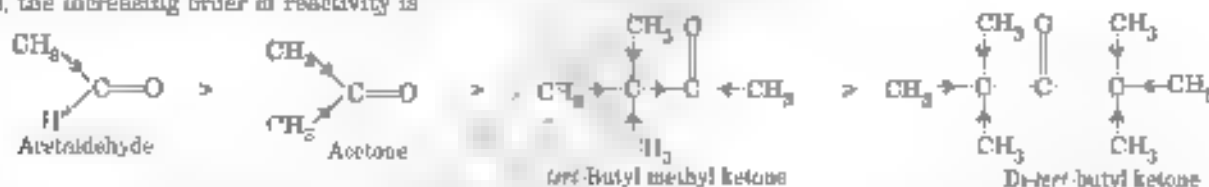
Q.1. An organic compound A (molecular formula $C_8H_{16}O_2$) was hydrolysed with dilute sulphuric acid to give a carboxylic acid (B) and an alcohol (C). Oxidation of (C) with chromic acid produced B (C on dehydration gives but-1-ene). Write equations for the reactions involved. A.I.S.B. 2009

- Ans.** a) Since the given compound on hydrolysis with dil. H_2SO_4 gives carboxylic acid B and an alcohol C it must be an ester.
 b) Since the oxidation of alcohol (C) gives the acid B, therefore both the carboxylic acid B and alcohol C must contain same number of C atoms.
 c) Since ester A contains 8 carbon atoms, therefore both carboxylic acid B and the alcohol C must contain 4 C atoms each.
 d) Alcohol C on dehydration gives but-1-ene and therefore C must be a straight chain alcohol i.e. butan-1-ol.
 e) B is obtained by the oxidation of (C) and therefore, B must be butanoic acid.
 This also suggests that the ester A must be butyl butanoate. The relevant reactions are



Q.12. Arrange the following compounds in increasing order of their property as indicated :

- i) Acetaldehyde, Acetone, Di-*tert*-butyl ketone, Methyl *tert*-butyl ketone (reactivity towards HCN)
 ii) $CH_3CH_2CH_2Br$, CH_3CH_2Br , CH_3COOH , $CH_3CH_2CH_2COOH$ (acid strength)
 iii) Benzoic acid, 4-Nitrobenzoic acid, 3,4-Dinitrobenzoic acid, 4-Methoxybenzoic acid (acid strength)
Ans. The reactivity towards HCN addition decreases as + effect of 'alkyl' group or groups increases and/or the steric hindrance to the nucleophilic attack by CN^- at the carbonyl carbon increases.
 Thus, the increasing order of reactivity is



- i. We know that +I effect decreases the acid strength of carboxylic acid while -I effect increases the acid strength of carboxylic acid. The +I effect of isopropyl group is more than that of *n*-propyl group, therefore, $CH_3CH(CH_3)COOH$ is a weaker acid than $CH_3CH_2CH_2COOH$.

Since -I effect decreases with distance, therefore, $CH_3CH_2CH_2Br$ is a stronger acid than CH_3CH_2Br .
 Thus, the overall increasing order of acid strength is



- ii) Electron donating groups decrease the acid strength and therefore 4-methoxy benzoic acid is a weaker acid than benzoic acid.

Since electron withdrawing groups increase the acid strength therefore, both 4-nitrobenzoic acid and 3,4-dinitrobenzoic acids are stronger acids than benzoic acid. Further because of the presence of additional -NO₂ group at *m*-position with -CH=O group, 3,4-dinitrobenzoic acid is a little stronger acid than 4-nitrobenzoic acid. Thus the increasing order of acid strength is



Q.13 Give simple chemical tests to distinguish between the following pairs of compounds:

- i) Propanal and propanone
 ii) Phenol and Benzoic acid
 iii) Pentan-2-one and pentan-3-one
 iv) Ethanal and propanal
 v) Acetophenone and Benzophenone
 vi) Benzoic acid and Ethyl benzoate
 vii) Benzaldehyde and Acetophenone

Ans. (i) Propanal and propanone

- a) Propanal gives silver mirror with Tollen's reagent



Propanone does not give this test

- b Propanal gives red ppt. with Fehling solution, while propanone does not give this test



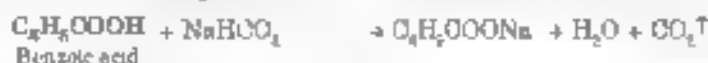
(ii) **Acetophenone and Benzophenone**

- a Acetophenone gives yellow ppt. with alkaline solution of iodine iodoform test. Benzophenone does not give this test



Phenol and Benzoic acid

- a Benzoic acid reacts with NaHCO_3 to give effervescence due to the evolution of CO_2

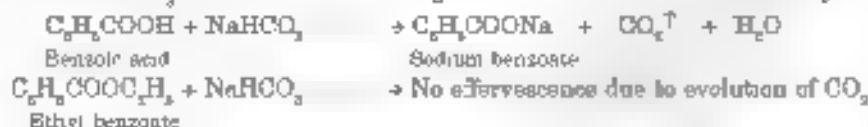


Phenol does not give effervescence

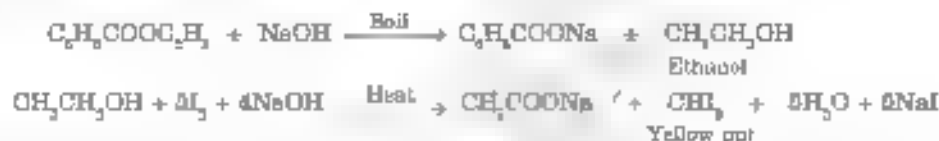
- b Phenol gives violet colour with FeCl_3 solution but benzoic acid does not give such colour

(iii) **Benzoic acid and ethyl benzoate**

- a When treated with NaHCO_3 solution benzoic acid gives brisk effervescence while ethyl benzoate does not



- b Ethyl benzoate on boiling with excess of NaOH gives ethyl alcohol which on heating with iodine gives yellow ppt. of iodoform



(iv) **Pentan-2-one and pentan-3-one**

- a Pentan-2-one forms yellow ppt. with alkaline solution of iodine iodoform test but pentan-3-one does not give iodoform test



- b Pentan-2-one gives white ppt. with sodium bisulphite while pentan-3-one does not give.



(v) **Benzaldehyde and Acetophenone**

- a Benzaldehyde forms silver mirror with ammoniacal silver nitrate solution Tollens reagent. Acetophenone does not react



- b Acetophenone forms yellow ppt. of iodoform with alkaline solution of iodine iodoform test. Benzaldehyde does not react



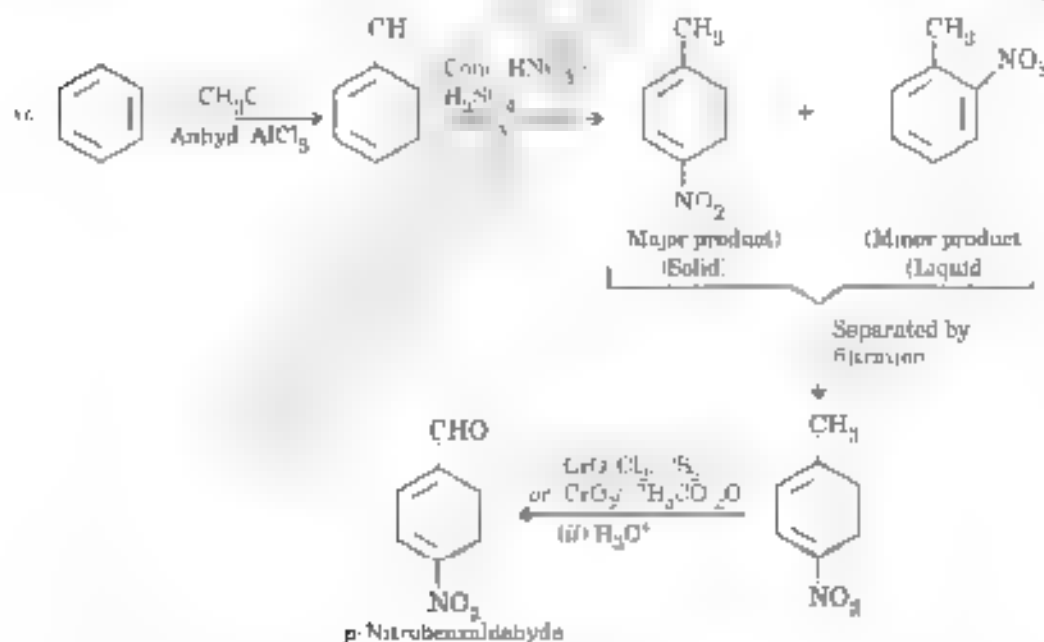
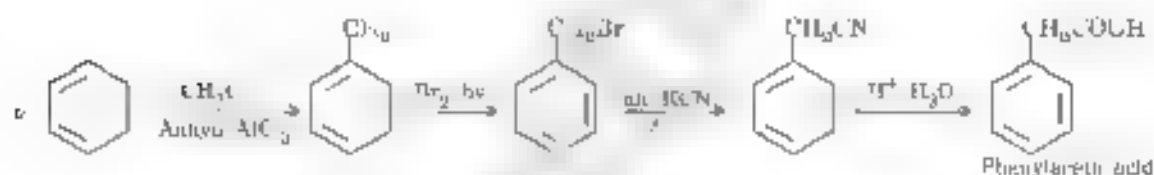
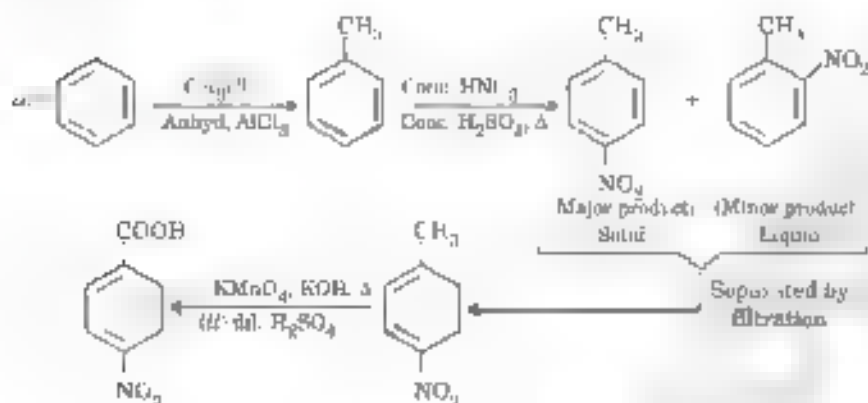
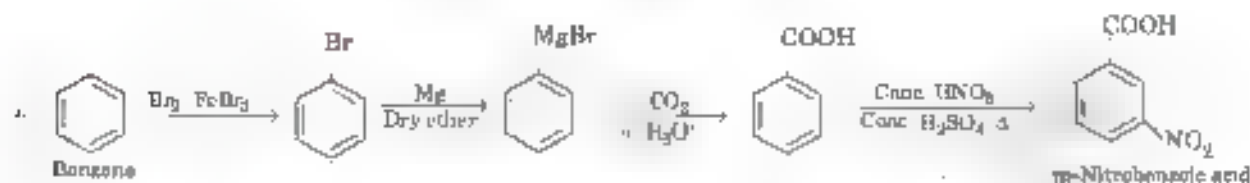
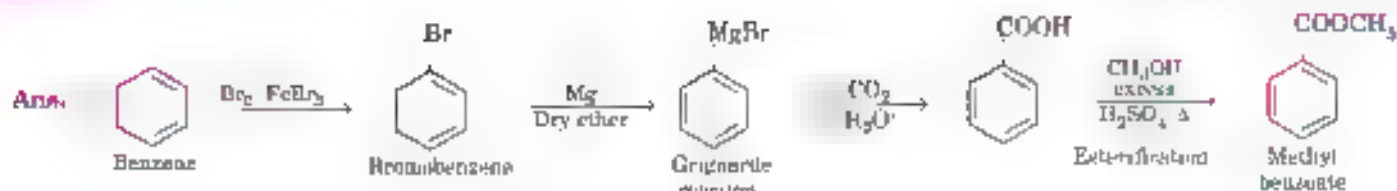
(vi) **Ethanal and propanal**

Ethanal gives yellow ppt. of iodoform with an alkaline solution of iodine iodoform test



Q.14. How will you prepare the following compounds from benzene? You may use any inorganic reagent and any organic reagent having not more than one carbon atom.

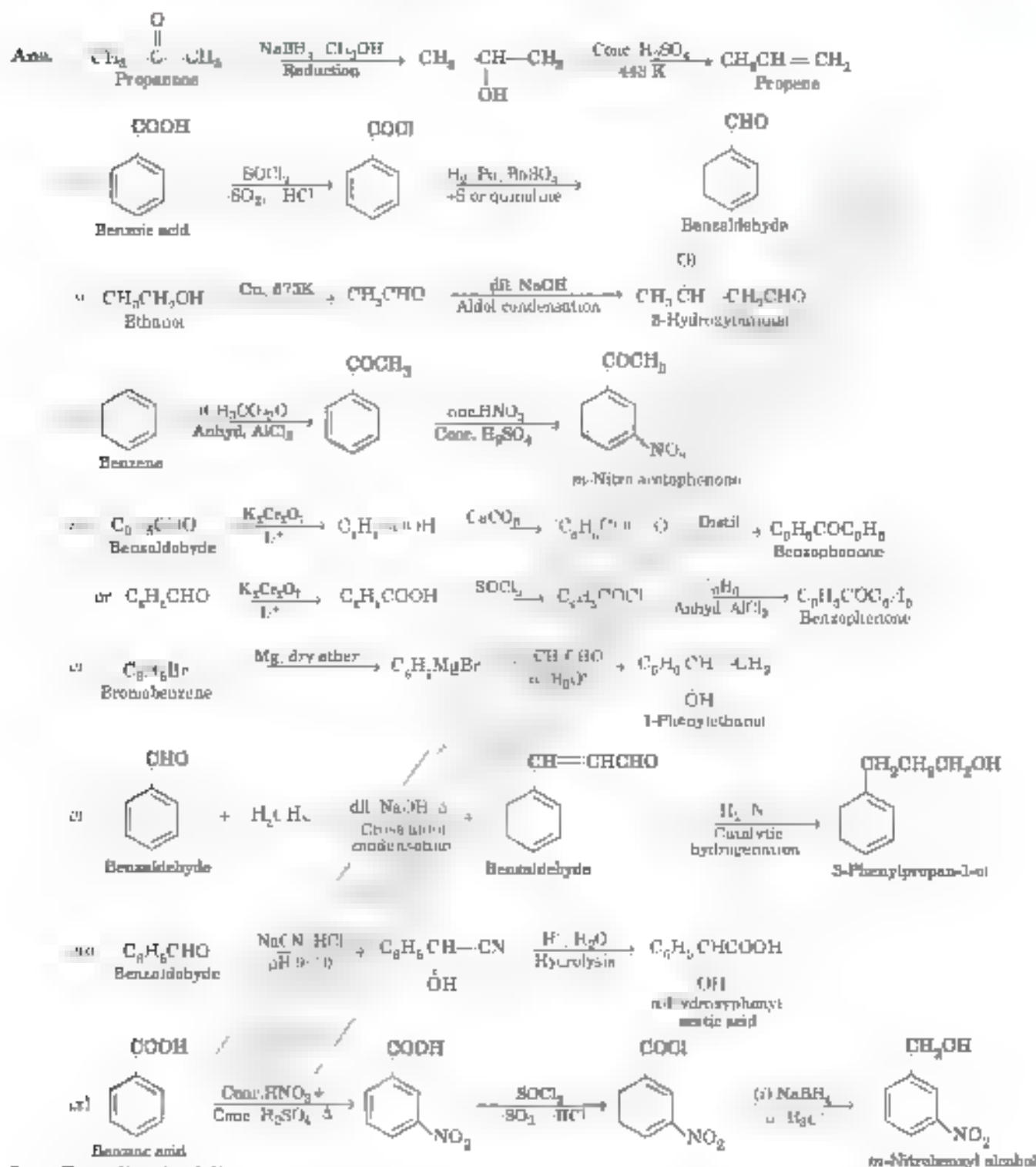
- (i) Methyl benzoate (ii) *m*-Nitrobenzoic acid (iii) *p*-Nitrobenzoic acid
(iv) Phenylacetic acid (v) *p*-Nitrobenzaldehyde



Q.16. How will you bring about the following conversions in not more than two steps?

- | | |
|-----------------------------------|--------------------------------------|
| (i) Propanone to propene | (ii) Benzoic acid to Benzaldehyde |
| (iii) Ethanol to 3-Hydroxybutanal | (iv) Benzene to m-Nitroacetophenone |
| (v) Benzaldehyde to Benzophenone | (vi) Bromobenzene to 1-Phenylethanol |

- (iii) Benzaldehyde to 3-Phenylpropan-1-ol (iv) Benzaldehyde to α -hydroxyphenylacetic acid
 (v) Benzoic acid to *m*-Nitrobenzyl alcohol

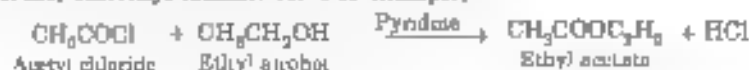


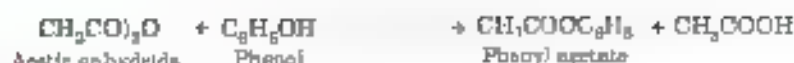
Q.10. Describe the following :

- (i) Acetylation (ii) Cannizzaro reaction (iii) Cross aldol condensation (iv) Decarboxylation

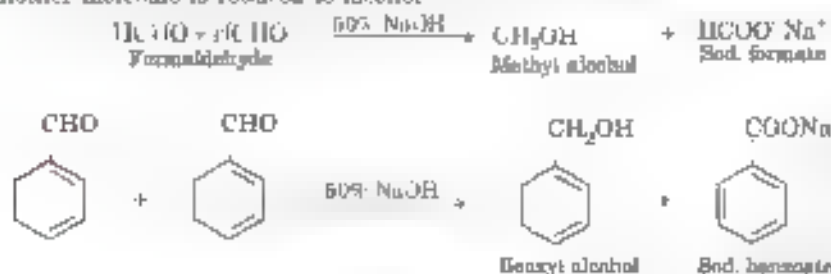
Ans. (i) Acetylation

The replacement of an active hydrogen of alcohols, phenols or amines with acetyl group to form corresponding esters or amides is called acetylation. It is carried out by using acid chlorides or anhydrides in the presence of a base such as pyridine, dimethyl aniline, etc. For example,

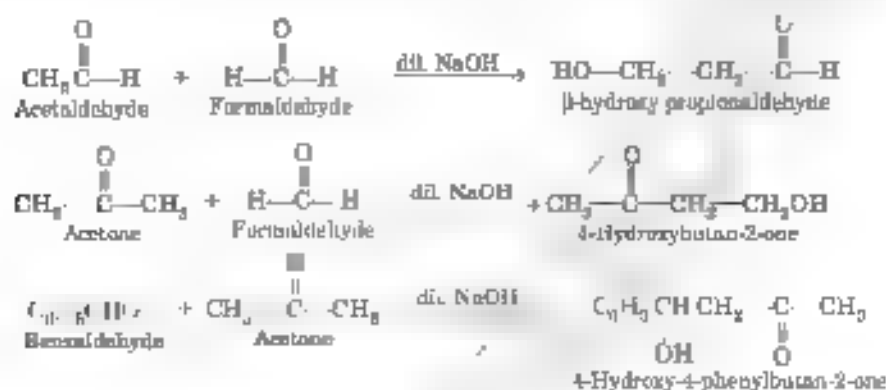


**Cannizzaro's reaction**

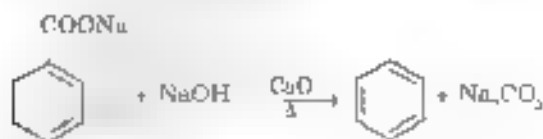
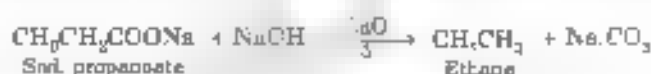
Aldehydes which do not contain any α -hydrogen atom e.g. benzaldehyde formaldehyde undergo self oxidation and reduction reaction on treatment with conc. solution of caustic alkali. In this reaction, one molecule is oxidised to acid while another molecule is reduced to alcohol.

**(iii) Cross aldol condensation**

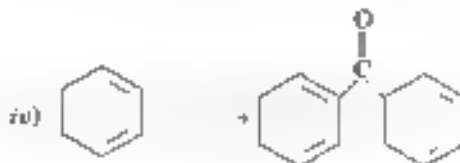
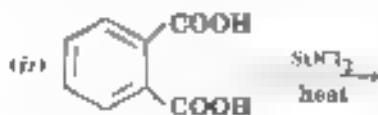
The condensation of two different molecules of aldehydes or ketones is called cross aldol condensation. It is useful synthetic reaction only if one of the aldehydes does not contain α -hydrogen atoms e.g. formaldehyde, benzaldehyde etc.

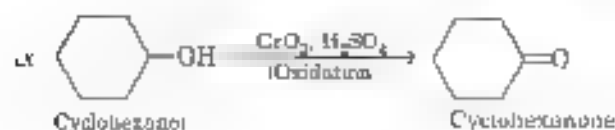
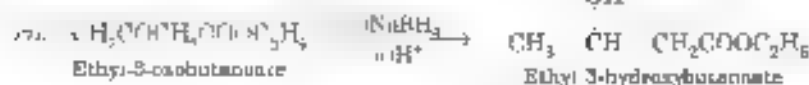
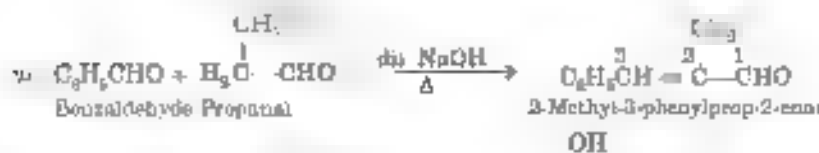
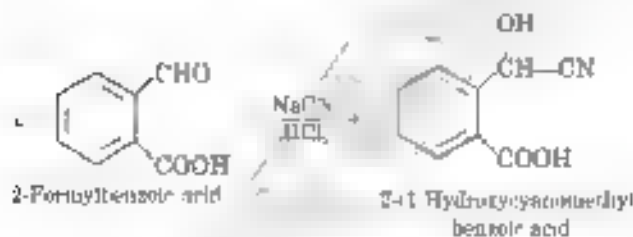
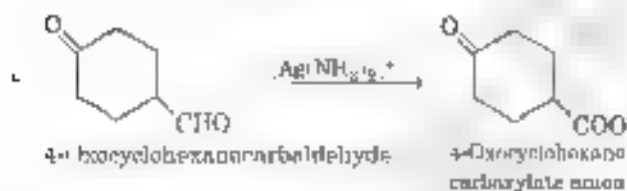
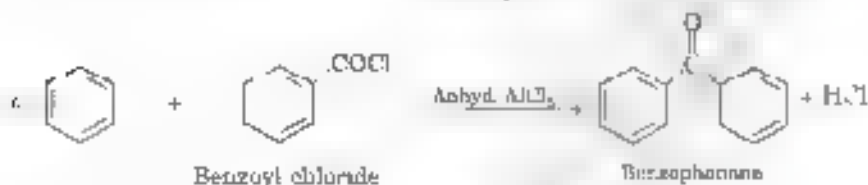
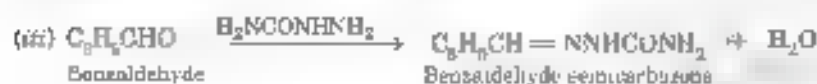
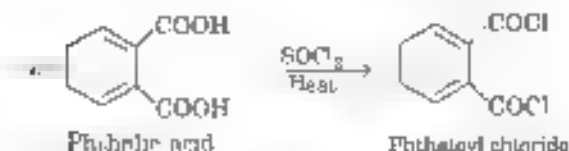
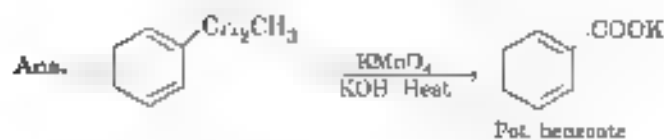
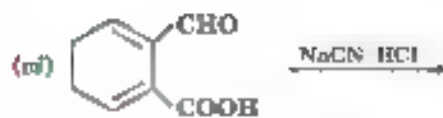
**(iv) Decarboxylation**

The process of removal of a molecule of CO_2 from a carboxylic acid is called decarboxylation. It is usually carried out by heating a mixture of a carboxylic acid or its sodium salt with soda lime ($\text{NaOH} + \text{CaO}$).

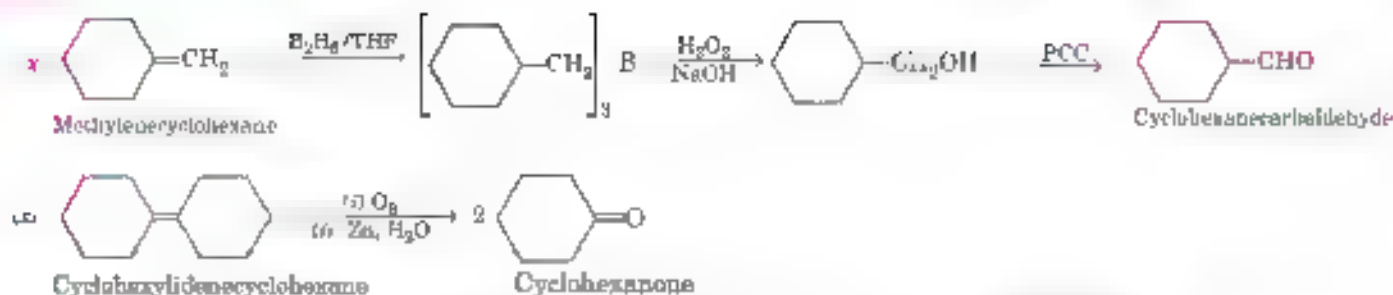


Q17 Complete each synthesis by giving missing starting material, reagent or products



**HELP**

Only aldehydes are oxidised by Tollen's reagent



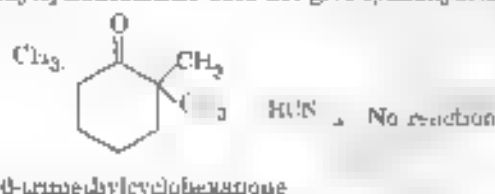
Q.18. Give plausible explanation for each of the following

- Cyclohexanone forms cyanohydrin in good yield but 2,2,6-trimethylcyclohexanone does not
- There are two -NH_2 groups in semicarbazide. However, only one is involved in the formation of semicarbazones.
- During the preparation of esters from a carboxylic acid and an alcohol in the presence of an acid catalyst, the water or the ester should be removed as soon as it is formed.

Ans. (i) Cyclohexanone forms cyanohydrin in good yield.



However, 2,2,6-trimethylcyclohexanone does not give cyanohydrin as



This is because of the presence of three methyl groups at α -position with respect to carbonyl group which hinder the nucleophilic attack of CN^- group due to steric hindrance. However, there is no such steric hindrance in cyclohexanone and therefore the nucleophilic attack by CN^- ion occurs readily to form cyanohydrin.

- (ii) Semicarbazide has two -NH_2 groups but one of these which is directly attached to C=O is involved in resonance as shown below



As a result of resonance, electron density on NH_2 group decreases and hence it does not act as a nucleophile. In contrast, the lone pair of electrons on the NH group is attached to NH is not involved in resonance and is therefore, available for nucleophilic attack on the C=O group of the aldehydes and ketones.

- (iii) The formation of esters from carboxylic acid and an alcohol in the presence of an acid catalyst is a reversible reaction.



Therefore, to shift the equilibrium in the forward direction, the water or ester formed should be removed as fast as it is formed.

Q.19. An organic compound contains 69.77% carbon, 11.63% hydrogen and rest oxygen. The molecular mass of the compound is 88. It does not reduce Tollens' reagent but forms an addition compound with sodium hydrogen sulphate and gives positive iodoform test. On vigorous oxidation it gives ethanoic and propanoic acid. Write the possible structure of the compound. (D.S.B. 2008, Assam S.B. 2019)

Ans. Step 1 To determine the molecular formula of the compound

$$\begin{aligned} \%C &= 69.77 & \%H &= 11.63 \\ \%O &= 100 - 69.77 + 11.63 = 18.60 \end{aligned}$$

Simple atomic ratio

$$\begin{aligned} \text{C : H : O} &= \frac{69.77}{12} : \frac{11.63}{1} : \frac{18.6}{16} \\ &= 5.88 : 11.63 : 1.16 \\ &= 5 : 10 : 1 \end{aligned}$$

Empirical formula = $\text{C}_5\text{H}_{10}\text{O}$

$$\text{Empirical formula mass} = 5 \times 12 + 10 \times 1 + 1 \times 16 = 86$$

$$\text{Molecular formula mass} = 86$$

$$n = \frac{\text{Molecular formula mass}}{\text{E.F. mass}}$$

$$= \frac{86}{86} = 1$$

$$\text{Molecular formula} = \text{C}_5\text{H}_{10}\text{O}$$

Step 2 Determining the structure of the compound

Since the given compound forms sodium hydrogen sulphite addition product, it must be an aldehyde or a ketone.

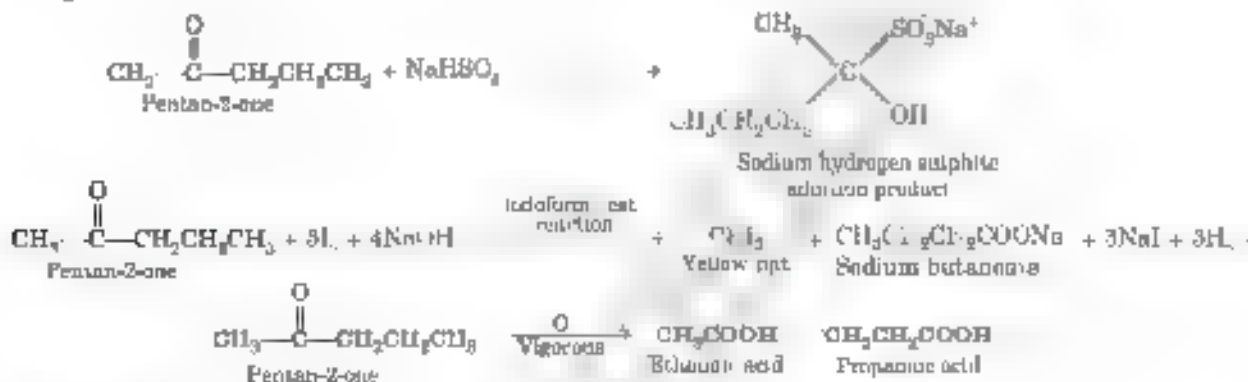
Since the compound does not reduce Tollen's reagent, therefore, it cannot be an aldehyde and must be a ketone.

Since the compound gives iodoform test, therefore, the compound must be methyl ketone.

Since the compound on vigorous oxidation gives a mixture of ethanoic acid and propanoic acid, therefore the methyl ketone is pentan-2-one i.e.

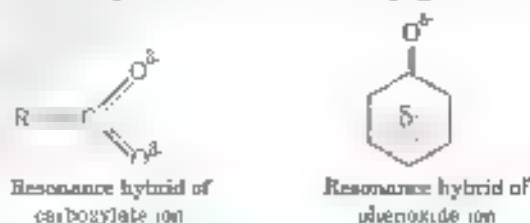


The given reactions are



Q.20. Although phenoxide ion has more number of resonating structure than carboxylate ion, carboxylic acid is a stronger acid than phenol. Why?

Ans. The phenoxide ion has more number of resonating structures but carboxylic acid is more stronger acid than phenol. Since there are two electronegative oxygen atoms in carboxylate ion as compared to only one oxygen atom in phenate ion, therefore, the electron charge on the carboxylate ion is more dispersed in comparison to phenate ion. Consequently carboxylate ion is relatively more stable as compared to phenate ion. Thus the release of H^+ ion from carboxylic acid is comparatively easier and therefore, it behaves as stronger acid than phenol. *For details refer page 71.*



NCERT

Exemplar Problems

Subjective Questions

2. Write a test to differentiate between pentan-2-one and pentan-3-one.

Ans. Pentan-2-one forms yellow ppt. with alkaline solution of iodine (iodoform test) but pentan-3-one does not give iodoform test.

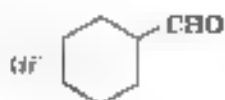
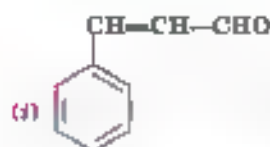


Short Answer Type Questions

1. Why is there a large difference in the boiling points of butanol and butan-1-ol?

Ans. Butan-1-ol has higher boiling point due to intermolecular hydrogen bonding.

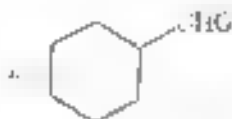
3. Give the IUPAC names of the following compounds



Ans.



3-Phenyl prop-2-enal



Cyclohexanecarbaldehyde



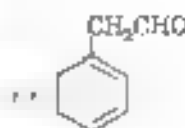
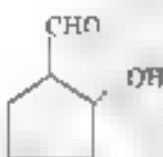
4. Give the structure of the following compounds.

(i) 4-Nitropropophenone

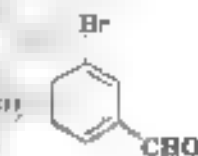
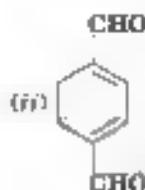
(ii) 2-Hydroxycyclopentanecarbaldehyde

(iii) Phenyl acetaldehyde

Ans.



5. Write IUPAC names of the following structures.



Ans.

Ethane-1,2-dial

Benzene-1,4-dicarbaldehyde

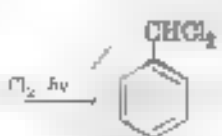
3-Bromobenzaldehyde

6. Benzaldehyde can be obtained from benzal chloride. Write reactions for obtaining benzaldehyde and then benzaldehyde from it.

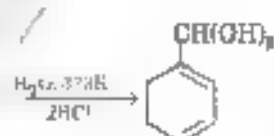
Ans.



Toluene



Benzal chloride



Benzaldehyde

7. Name the electrophile produced in the reaction of benzene with benzoyl chloride in the presence of anhydrous AlCl_3 . Name the reaction also.

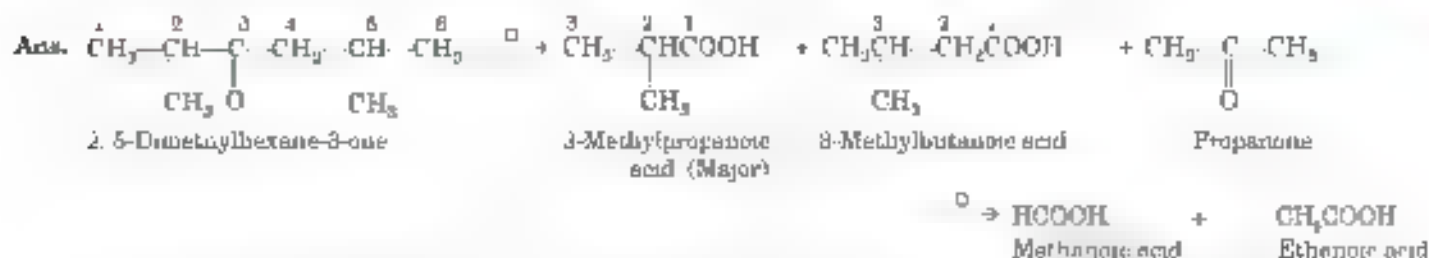
Ans.

$\text{C}_6\text{H}_5\text{CO}^+$ Benzoyl cation

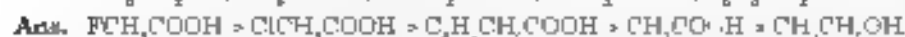


Friedel-Crafts acylation reaction.

8. Oxidation of ketones involves carbon-carbon bond cleavage. Name the products formed on oxidation of 2, 5-dimethylhexan-3-one.

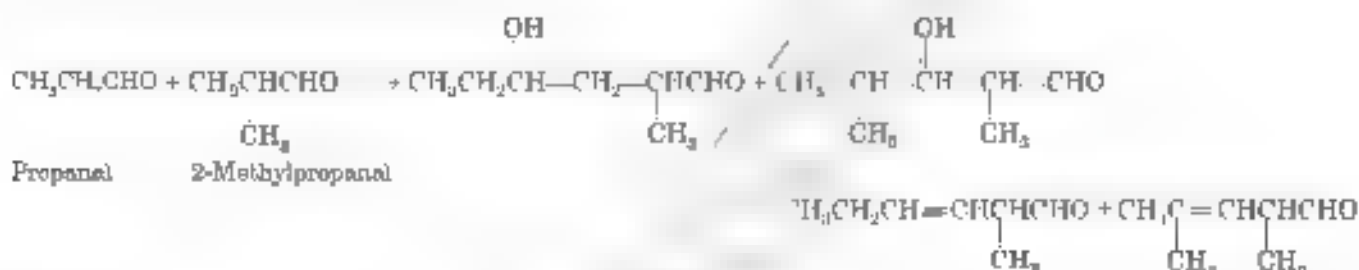


9. Arrange the following in decreasing order of their acidic strength and give reason for your answer.



10. What product will be formed on reaction of propanal with 2-methylpropanal in the presence of NaOH? What products will be formed? Write the name of the reaction also.

Ans. It is cross aldol-condensation reaction.



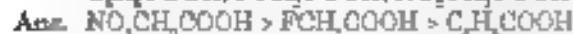
11. Compound 'A' was prepared by oxidation of compound 'B' with alkaline KMnO_4 . Compound 'A' on reduction with lithium aluminium hydride gets converted back to compound 'B'. When compound A is heated with compound B in the presence of H_2SO_4 it produces fruity smell of compound 'C' to which family the compounds 'A', 'B' and 'C' belong to?

Ans. A is carboxylic acid

B is an ethanol

C is an ester

12. Arrange the following in decreasing order of their acidic strength. Give explanation for the arrangement.



This is due to electron withdrawing effect.

13. Alkenes ($>\text{C}=\text{C}<$) and carbonyl compounds ($>\text{C}=\text{O}<$), both contain a π bond but alkenes show electrophilic addition reactions whereas carbonyl compounds show nucleophilic addition reactions. Explain.

Ans. Carbonyl group is polar in nature due to larger electronegativity of oxygen as compared to carbon. Carbon acquires partial positive charge while O acquires partial negative charge.



Because of slight positive charge on C atom, it is attacked by nucleophiles and therefore undergoes nucleophilic addition reaction.

Ethylene double bond is a non-polar bond and is a source of electrons. Therefore it is attacked by electrophiles and undergoes electrophilic addition reactions.

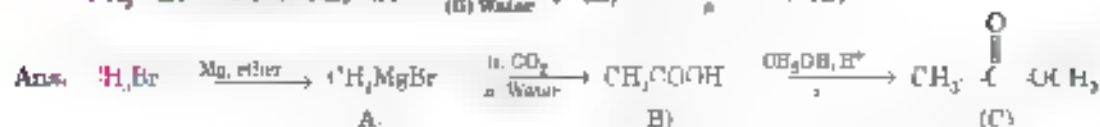
14. Carboxylic acids contain carbonyl group but do not show the nucleophilic addition reaction like aldehydes or ketones. Why?

Ans. Carboxylic acids do not give the characteristic reactions of carbonyl group ($\text{C}=\text{O}$) as given by aldehydes and ketones. In carboxylic acids, the carbonyl group is involved in resonance, as follows



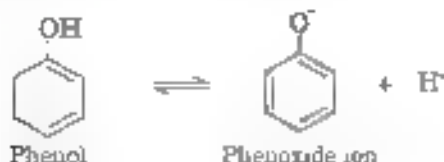
Therefore, it is not a free group. But no resonance is possible in aldehydes and ketones. They give the characteristic reactions of the group.

15. Identify the compounds A, B and C in the following reaction.

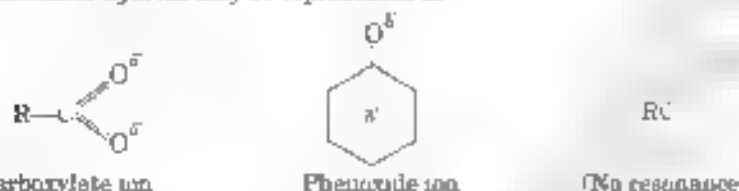


16. Why are carboxylic acids more acidic than alcohols or phenols although all of them have hydrogen atom attached to an oxygen atom (—O—H)?

Ans. The aliphatic carboxylic acids are stronger acids than alcohols and phenols. The difference in the relative acids strengths can be understood if we compare the resonance hybrids of carboxylate ion and ethoxide phenoxide ion.

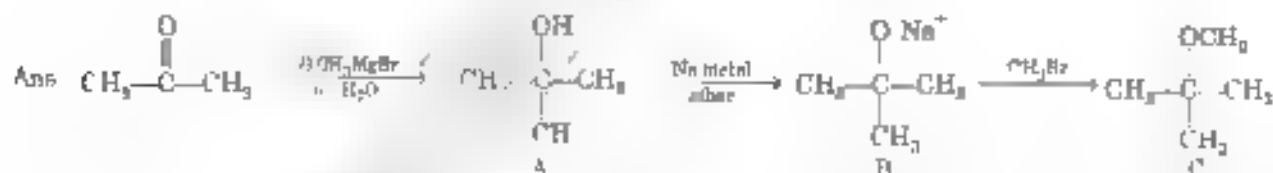


The resonance hybrids may be represented as



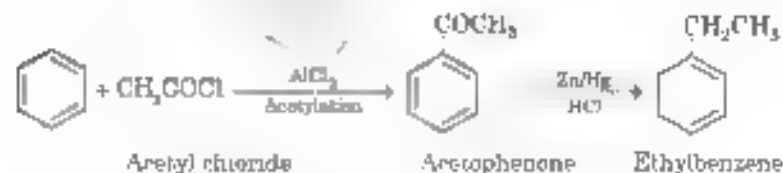
The electron charge on the carboxylate ion is more dispersed in comparison to the phenate ion since there are two electronegative oxygen atoms in carboxylate ion as against the only one oxygen atom in phenoxide ion. In other words, the carboxylate ion is relatively more stable as compared to phenate ion. This is the reason why the release of H^+ ion from carboxylic acid is comparatively easier or it behaves as a stronger acid than phenol.

17. Complete the following reaction sequence



18. Ethylbenzene is generally prepared by acetylation of benzene followed by reduction and not by direct alkylation. Think of a possible reason.

Ans. Ethyl benzene is prepared as

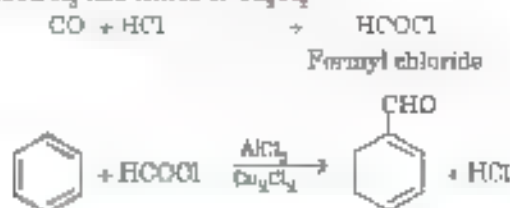


The direct alkylation does not give pure product



10. Can Gatterman-Koch reaction be considered similar to Friedel-Craft's acylation? Discuss.

Ans. In Gatterman-Koch reaction, benzene is converted to benzaldehyde by passing a mixture of CO and HCl gas in the presence of anhydrous AlCl_3 and traces of Cu_2Cl_2 .



This reaction is a modification of Friedel-Craft's reaction in which $-\text{CHO}$ group is introduced in the benzene ring.



Quick

MEMORY TEST



A. Say True or False

- Aldehydes and ketones react with electrophiles but not with nucleophiles.
- Wolff-Kishner reduction of acetophenone gives toluene.
- Acetaldehyde can be prepared by the distillation of calcium acetate.
- Acetaldehyde can be reduced to ethane in the presence of LiAlH_4 .
- Benzaldehyde cannot undergo Cannizzaro reaction.
- Aldehydes are less easily oxidised than ketones.
- Acetaldehyde cyanohydrin on hydrolysis gives acetic acid.
- Benzaldehyde reduces Fehling solution.
- Benzaldehyde forms addition product with sodium bisulphite but acetophenone does not.
- Ketones give nucleophilic addition reactions more readily than aldehydes.
- Calcium formate on heating gives acetaldehyde.
- The pK_a value of formic acid is smaller than that of acetic acid.
- The carbon-oxygen bond lengths in formic acid are equal.
- Nitration of benzoic acid gives *m*-nitrobenzoic acid.
- During the reaction of carboxylic acid with NaHCO_3 , the carbon of the CO_2 produced comes from NaHCO_3 .
- When benzoic acid is heated with soda lime, benzene is formed.
- Acetate ion is a stronger acid than methoxide ion.
- Ethanoic acid liberates hydrogen with sodium metal.
- $\text{Me}_3\text{CCH}_2\text{COOH}$ is more acidic than $\text{Me}_3\text{SiCH}_2\text{COOH}$.
- Formic acid gives silver mirror test with Tollen's reagent.

B. Complete the missing links

- Aldehydes form red precipitate with Fehling solution if _____.
- In carbonyl compounds the carbon atom involves _____ hybridisation.
- The IUPAC name of propanaldehyde is _____.
- The oxidation of toluene with _____ gives benzaldehyde.
- Ketones on reduction with _____ amalgam and water form pinacols.

- Three moles of acetone on refluxing with conc. H_2SO_4 give _____.
- Acetone reacts with hydroxylamine to form _____.
- 2-Pentanone can be distinguished from 3-pentanone by _____.

2. Ammonia reacts with _____ to give urotropine.

10. When but-2-yne is hydrated with conc. H_2SO_4 in the presence of HgSO_4 , it gives _____.

11. $\text{CH}_3\text{CHO} + \text{HCHO} \xrightarrow{\text{dil. NaOH}}$ _____.

12. $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3 \xrightarrow[\text{glycol}]{\text{KMnO}_4/\text{H}_2\text{SO}_4/\text{heat}}$ _____ + H_2O

13. $\text{C}_6\text{H}_5\text{COCH}_3 + \text{H} \xrightarrow{\text{Zn/Hg, HCl}}$ _____ + H_2O

14. $(\text{CH}_3)_2\text{CO} + \text{NaHSO}_3 \rightarrow$ _____

15. $\text{C}_6\text{H}_5\text{CHO} + (\text{CH}_3)_2\text{CHO} \xrightarrow[\text{HCl}]{\text{dil. NaOH}}$ _____

16. Carboxylic acids may be prepared by reacting Grignard reagents with _____.

17. Kolbe's electrolysis of potassium succinate gives carbon dioxide and _____.

18. _____ is produced on heating ammonium acetate.

19. Hydrolysis of HCN gives _____.

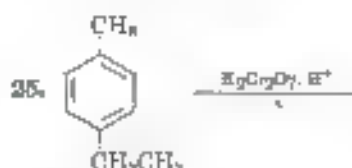
20. The lowest molecular mass monocarboxylic acid containing a secondary carbon atom is _____.

21. Trimethylacetic acid has _____ pK_a value than trifluoroacetic acid.

22. Ethyl acetate is reduced with LiAlH_4 to give _____.

23. Benzoic acid reacts with conc. H_2SO_4 in the presence of SO_3 to give _____ and water.

24. Propyl benzoic acid on oxidation gives _____.



C. Choose the correct alternative

- When calcium acetate is distilled with calcium formate, the product obtained is acetone, acetaldehyde.

2. Benzoyl chloride on reduction with hydrogen in the presence of Pd and BaSO₄ gives acetophenone/benzaldehyde
3. The boiling point of propanoic acid is higher/lower than that of propane.
4. Aldehydes and ketones undergo nucleophilic/electrophilic addition reactions
5. Acetaldehyde reacts with DNP to give orange/black precipitate
6. Aldehydes and ketones react with ammonium derivatives in weakly acidic/strongly acidic medium
7. The red brown precipitate of aldehydes with Fehling solution is due to formation of Cu₂O/CuO
8. Iodoform test is given by ethanal/propanal
9. Aldehydes or ketones are reduced to alkanes/alcohols with NaBH₄
10. On cooling acetaldehyde with a few drops of conc. H₂SO₄ at 0°C, the product formed is paraldehyde/metalddehyde.
11. The reaction $\text{CH}_3-\text{CH}_3 + \text{CO} + \text{H}_2\text{O}$ (steam) $\xrightarrow{\text{H}_2\text{PtCl}_6, \Delta}$ $\text{CH}_3\text{CH}_2\text{COOH}$ is known as Koch reaction/Mendius reaction
12. During the reaction of carboxylic acid with Na₂CO₃, the carbon dioxide evolved comes from Na₂CO₃/carboxylic acid
13. pK_a value of m-hydroxybenzoic acid is less/more than that of benzoic acid
14. Carboxylic acids are reduced to alkanes/alcohols with HI/red P
15. When calcium acetate is distilled, it gives acetone/acetaldehyde
16. Formic acid/gases, does not give silver mirror with Tollen's reagent.
17. Carboxyl group in benzoic acid is o-and p/m-director
18. o-hydroxy benzoic acid is less/more acidic than p-hydroxy benzoic acid
19. Boiling points of carboxylic acids are less/more than the corresponding alcohols
20. Chloroacetic acid reacts with KCN followed by acidic hydrolysis to give malonic acid/lactic acid.

Answers

Quick

MEMORY TEST



A. Ray True or False

1. False. Aldehydes and ketones react with both nucleophiles/bases and electrophiles/acids
2. False. It forms ethyl benzene
3. False. Distillation of calcium acetate gives acetone
4. False. Ethyl alcohol is formed. 5. False 6. False
7. True 8. False 9. True 10. False
11. False. It gives formaldehyde
12. True 13. False 14. True
15. True 16. True
17. False. Acetate ion is a weaker base than methoxide ion because a stronger acid has a weaker conjugate base
18. True 19. True 20. True

B. Complete the table/blank

1. sp^2 2. sp^3
3. But-2-enal 4. chromyl chloride in CS₂
5. magnesium 6. mesitylene
7. acetoxime ($\text{CH}_3\text{CH}=\text{N}-\text{OH}$)
8. Iodoform test 9. formaldehyde
10. butan-2-one 11. $\text{HO}-\text{CH}_2\text{CH}_2\text{CHO}$

12. $\text{CH}_3\text{CH}_2\text{CH}_3$ 13. $\text{C}_6\text{H}_5\text{CH}_2\text{CH}_3$ 14. $\text{CH}_3\text{C} \begin{smallmatrix} \text{OH} \\ \text{SO}_3\text{Na} \end{smallmatrix}$ 15. $\text{C}_6\text{H}_5\text{CH}=\text{CH}-\text{CHO}$

16. carbon dioxide

17. ethylene

18. Acetamide

19. formic acid

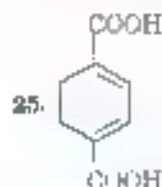
20. 2-Methyl propanoic acid

21. higher

22. ethyl alcohol

23. 3-sulphobenzoic acid

24. benzoic acid

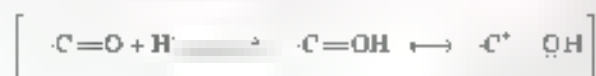


C. Choose the correct alternative

1. acetaldehyde 2. benzaldehyde 3. higher
4. nucleophile 5. orange 6. weakly acidic
7. Cu₂O 8. ethanal 9. alcohols
10. metalddehyde 11. Koch reaction 12. Na₂CO₃
13. less 14. alkanes 15. acetone
16. gives 17. m- 18. more
19. more 20. malonic acid

HOTS**Higher Order Thinking Skills & Advanced Level****QUESTIONS WITH ANSWERS****Q.1. Hydrazones of acetaldehyde are not prepared in highly acidic medium. Explain.**

Ans. In weakly acidic medium, the carbonyl group is protonated. As a result of presence of +ve charge on carbon, the protonated carbonyl group undergoes nucleophilic attack of hydrazine easily



In strongly acidic medium the hydrazine being basic in nature forms its salt by protonating the unshared pair of electrons on N atom.



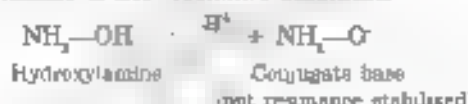
The salt cannot act as nucleophile. Thus, to carry out these reactions, we have to control the pH between 5 and 6.

Q.2. Oximes are more acidic than hydroxylamine. Explain.

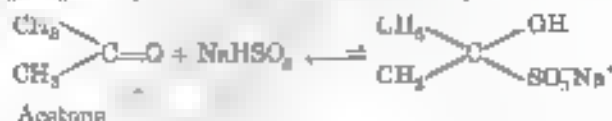
Ans. Oximes lose a proton to form a conjugate base which is stabilised by resonance.



On the other hand, conjugate base of hydroxylamine is not resonance stabilised.

**Q.3. Di-tert-butylketone does not give precipitate with NaHSO_3 , whereas acetone does. Explain.**

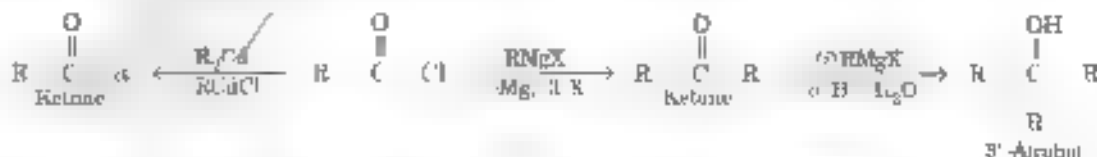
Ans. Acetone reacts with NaHSO_3 to give crystalline sulphonic acid addition product



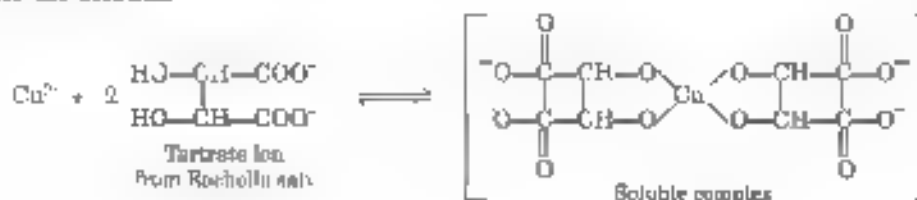
But di-tert-butyl ketone does not give a precipitate because of steric hindrance by bulky tert-butyl groups. Bisulphite ion cannot approach the carbon of the carbonyl group for addition.

Q.4. Explain why dialkyl cadmium is considered superior to Grignard reagent for the preparation of a ketone from an acid chloride.

Ans. Dialkyl cadmium is less reactive than Grignard reagent because cadmium is less electropositive (electronegativity = 1.7) than magnesium (electronegativity = 1.2). Therefore dialkyl cadmium reacts with more reactive acid chlorides to give ketones but doesn't react further with less reactive ketones so formed to give tert-alcohols. But Grignard reagents being more reactive not only react with acid chlorides but also with ketones formed to give tert-alcohols.

**Q.5. What is the function of Rochelle salt in Fehling's solution ?**

Ans. In alkaline medium, Cu^{2+} ions get precipitated as $\text{Cu}(\text{OH})_2$. To keep Cu^{2+} ions in solution in alkaline medium, Rochelle salt is added. This combines with insoluble $\text{Cu}(\text{OH})_2$ to form a soluble complex between Cu^{2+} ions and tartrate ion (from Rochelle salt) and therefore goes into the solution.



Q.6. Aldehydes usually don't form stable hydrates but chloral normally exists as chloral hydrate. Explain.

Ans. The addition of water to aldehydes is a reversible reaction in which the equilibrium lies almost towards left.



On the other hand, in chloral, the presence of three electron withdrawing Cl atoms increases the +ve charge on the carbonyl carbon. As a result weak nucleophiles like water readily add to the carbonyl group forming chloral hydrate and therefore, shift the equilibrium towards right.



Q.7 Treatment of $\text{C}_6\text{H}_5\text{CHO}$ with HCN gives a mixture of two isomers which cannot be separated even by very careful fractional distillation.

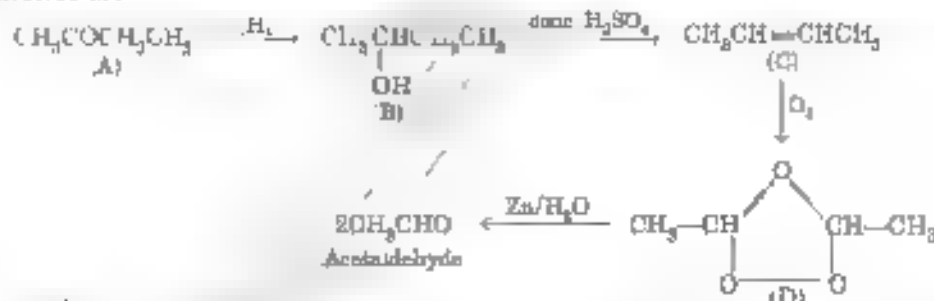
Ans. $\text{C}_6\text{H}_5\text{CHO}$ reacts with H^+CN^- to form two isomers benzaldehyde cyanohydrins because an asymmetric carbon atom is introduced.



These two isomers are enantiomers and therefore cannot be separated by physical methods like fractional distillation.

8. A ketone (A) which undergoes haloform reaction gives compound (B) on reduction. B on heating with conc. H_2SO_4 gives a compound (C) which forms monooxide (D). D on hydrolysis in the presence of zinc dust gives only acetaldehyde. Identify A, B, C and D. Write down the reactions involved.

Ans. A: $\text{CH}_3\text{COCH}_2\text{CH}_3$, Butan-2-one, B: $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$, Butan-2-ol and C: $\text{CH}_3\text{CH}=\text{CHCH}_3$, But-2-ene
The equations involved are

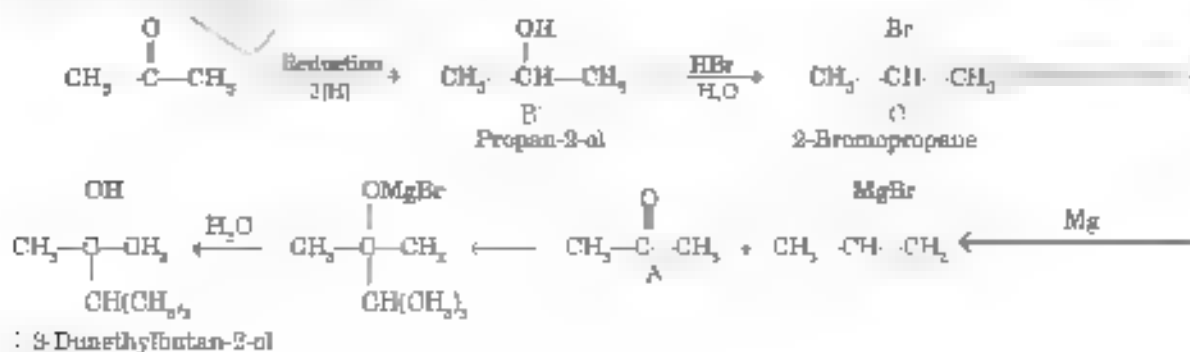


A gives haloform reaction as



9. An organic compound A ($\text{C}_6\text{H}_{10}\text{O}$) is resistant to oxidation but forms compound B ($\text{C}_6\text{H}_{10}\text{O}$) on reduction which reacts with HBr to form the bromide (C). C forms a Grignard reagent which reacts with A to give D ($\text{C}_{12}\text{H}_{20}\text{O}$). Give the structures of A, B, C and D and explain the reactions involved.

Ans. The compound A can be either an aldehyde or a ketone. Since it resists oxidation, it must be a ketone i.e. acetone CH_3COCH_3 .
The reactions involved are

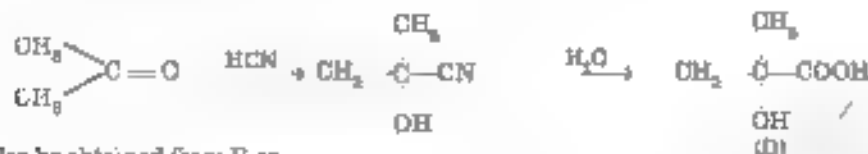


10. An alkene (A) on ozonolysis gives acetone and an aldehyde. The aldehyde is easily oxidised to an acid (B). When B is treated with bromine in the presence of phosphorus, it yields compound (C) which on hydrolysis gives a hydroxy acid (D). This acid can also be obtained from acetone by the reaction with hydrogen cyanide followed by hydrolysis. Identify the compounds A, B, C and D.

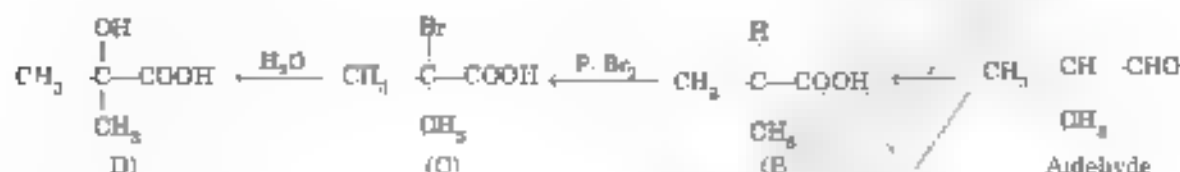
Ans. A gives acetone and an aldehyde (RCHO):



The nature of aldehyde can be established by its product D.



D can also be obtained from B as



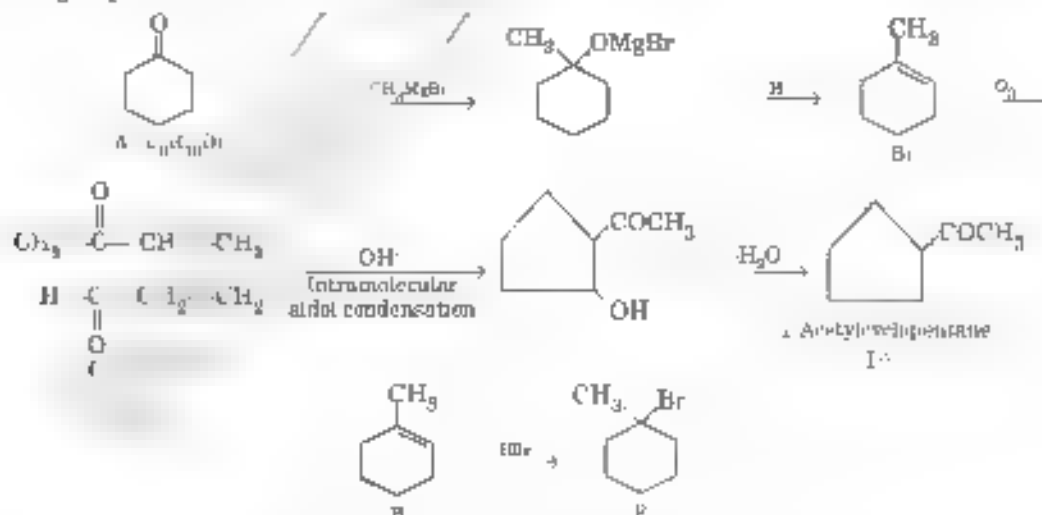
Thus, A is



11. An organic compound A, $\text{C}_8\text{H}_{10}\text{O}$, on reaction with CH_3MgBr followed by acid treatment gives compound B. The compound B on ozonolysis gives compound C, which in presence of a base gives 1-acetyl cyclopentane, D. The compound B on reaction with HBr gives compound E. Write the structures of A, B, C, D and E. Show how D is formed from C.

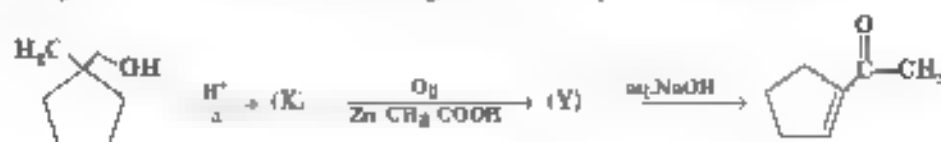
(I.I.T 2000)

Ans. The C and H ratio of A indicates that it is a cyclic compound. The reaction of A with CH_3MgBr indicates that it should have a ketonic group. The reactions are



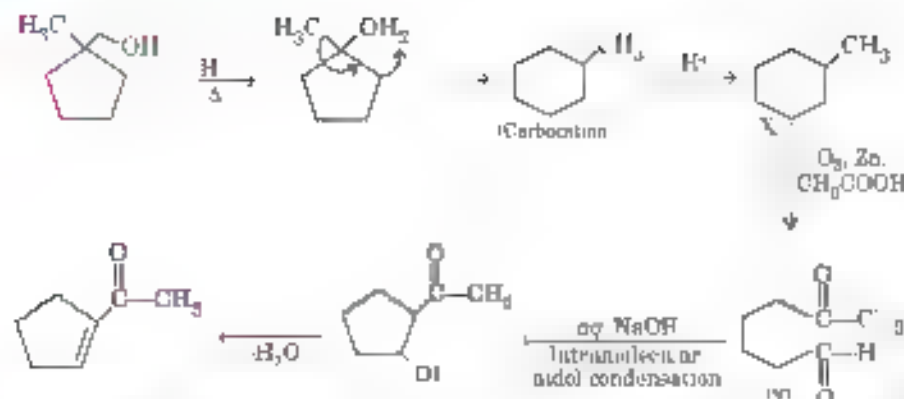
D is formed from C by intramolecular condensation of a dicarbonyl compound with a base forming a cyclic compound.

12. Identify (X) and (Y) in the following reaction sequence :



(I.I.T 2005)

Ans.



13. Explain the fact that the C—O bond length in RCOOH is shorter than in ROH

Ans. RCOOH has the following resonance structures



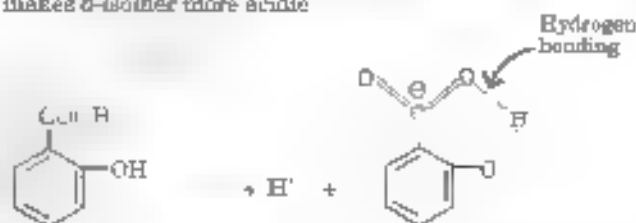
Because of the contribution of structure II, there is some double bond character in the C—O bond of the acid. Therefore, C—O bond length is shorter than in R—OH which has only C—O single bond.

14. Highly branched carboxylic acids are less acidic than unbranched acids. Why?

Ans. The carboxylate ion RCOO⁻ of branched carboxylic acids is shielded from solvent molecules and, therefore, cannot be stabilized by solvation as effectively as the carboxylate ion of unbranched acids.

15. Although *p*-hydroxy benzoic acid is less acidic than benzoic acid, *ortho* hydroxy benzoic acid (salicylic acid) is about 15 times more acidic than benzoic acid. Explain.

Ans. OH group is electron releasing group and, therefore, it increases the negative charge on the anion. As a result, *p*-hydroxy benzoic acid is less acidic than benzoic acid. However, *o*-hydroxy benzoic acid is more acidic than benzoic acid. The enhanced acidity of *o*-isomer is due to a very effective intramolecular hydrogen bonding in the carboxylate ion. As a result, *o*-hydroxy benzoate ion is stabilized to a great extent and, therefore, it makes *o*-isomer more acidic.



16. Fluorine is more electronegative than chlorine but *p*-fluorobenzoic acid is a weaker acid than *p*-chlorobenzoic acid. Explain.

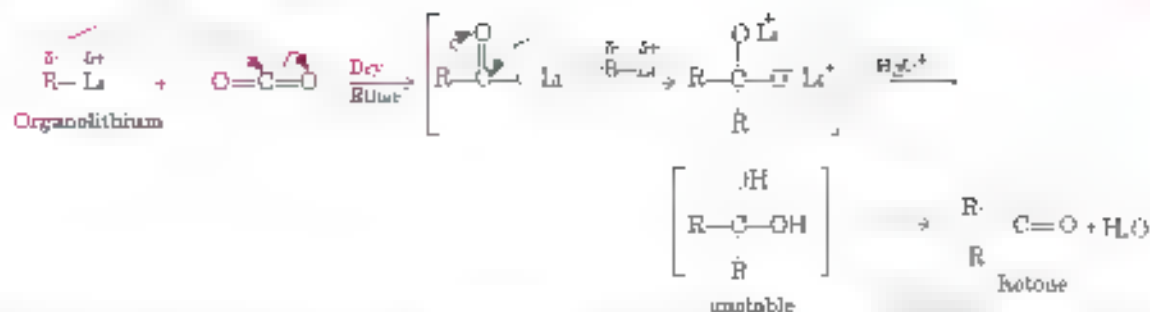
Ans. Halogens are more electronegative than carbon and also possess lone pairs of electrons. Therefore, halogens can exert -I and +R effects. In F atom, the lone pairs of electrons are present in 2*p*-orbitals but in Cl atom, they are present in 3*p*-orbitals. Since 2*p*-orbitals of F and C are of almost same size, therefore, +R effect is more pronounced in *p*-fluorobenzoic acid than in *p*-chlorobenzoic acid.



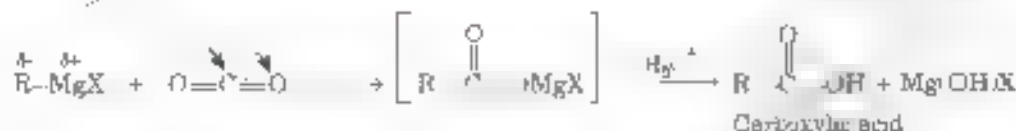
Thus, in *p*-fluorobenzoic acid, +R effect outweighs the -I effect and, therefore, it is weaker acid than *p*-chlorobenzoic acid having more -I effect than +R effect.

17. Addition of Grignard reagents to dry ice followed by hydrolysis gives carboxylic acids whereas that of organolithium compounds under similar conditions give ketones. Explain.

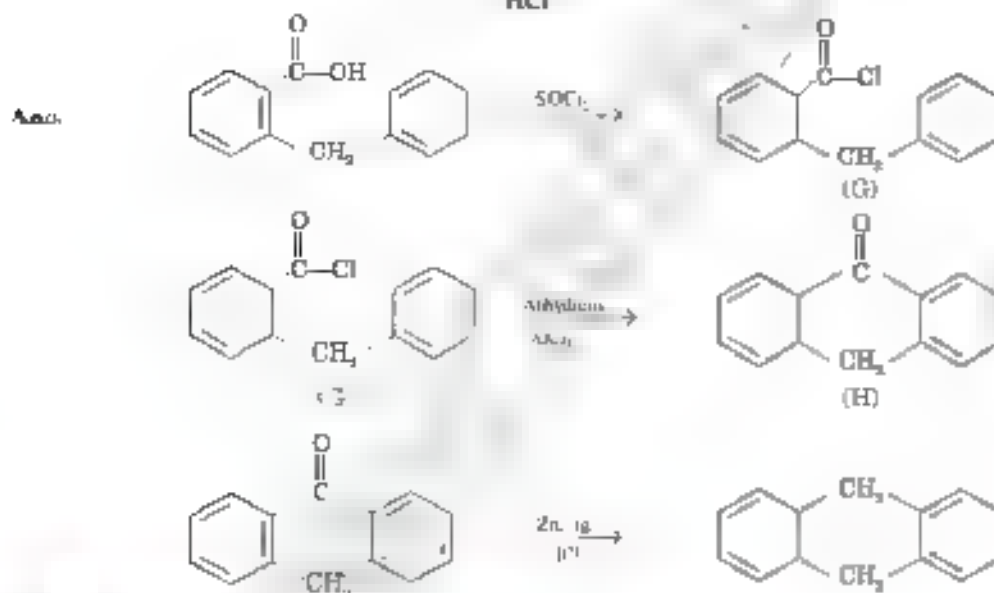
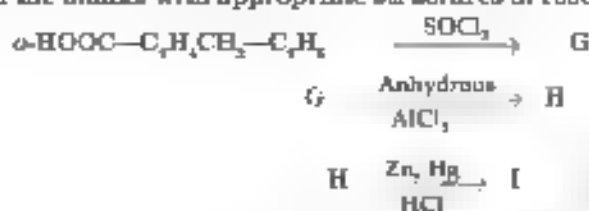
Ans. The electronegativity of Li (E.N. = 1.0) is lower than that of Mg (E.N. = 1.2) so that organolithium compounds are more nucleophilic than Grignard reagents. Therefore, organolithium compounds not only add to the more reactive CO₂, but also to less reactive resonance stabilized lithium salts of carboxylic acids forming ketones.



On the other hand, Grignard reagents are less nucleophilic and add only to $\text{C}=\text{O}$, but not to less reactive resonance stabilized magnesium salts of carboxylic acids from which the carboxylic acid can be generated by hydrolysis with mineral acids.



18. Fill in the blanks with appropriate structures of reaction products in the following transformations:



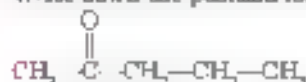
Revision Exercises

Very Short Answer Questions (carrying 1 mark)

- Arrange the following in order of their increasing reactivity towards HCN:
 CH_3CHO , CH_3COCH_3 , HCHO , $\text{C}_6\text{H}_5\text{COCH}_3$
 Karnataka S.B. 2014
- What is the hybridised state of carbonyl carbon atom?
 Karnataka S.B. 2014
- Give one chemical test to distinguish between pentan-2-one and pentan-3-one
 Assam S.B. 2013

- Give the structure and IUPAC name of an aliphatic aldehyde having two carbon atoms which undergoes Cannizzaro's reaction.

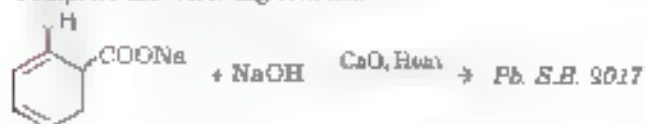
- Write down the product formed of



Pb S.B. 2017

- What happens when benzophenone is reduced with Zn/Hg in the presence of HCl ?

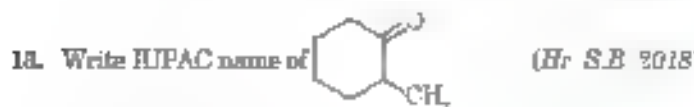
7. Draw the structure, formula of 1-phenylpropan-1-one molecule. (D.S.B. 2008)
 8. Complete the following reaction.



9. Arrange the following compounds in an increasing order of their reactivity in nucleophilic addition reactions: ethanal, propanal, propanone, butanone. (D.S.B. 2012)
 10. Arrange the following in the increasing order of their reactivity in nucleophilic addition reactions: $\text{C}_6\text{H}_5\text{CHO}$, $\text{C}_6\text{H}_5\text{COCH}_3$, $\text{C}_6\text{H}_5\text{COOC}_2\text{H}_5$. Meghalaya S.B. 2013
 11. Write the IUPAC name of



12. Write the IUPAC name of $(\text{CH}_3)_2\text{CHCHO}$ (Nagaland S.B. 2018)



14. What is Tollen's reagent? Ph. S.B. 2018
 15. Write the IUPAC name of the compound $\text{CH}_3-\underset{\text{NH}_2}{\text{CH}}-\text{CH}_2-\text{CHO}$ (D.S.B. 2014)

16. Write the IUPAC name of the compound $\text{CH}_3-\underset{\text{OH}}{\text{CH}}-\text{CH}_2-\overset{\text{O}}{\underset{\text{O}}{\text{C}}}-\text{CH}_3$ (D.S.B. 2014)

17. Arrange the following in the increasing order of boiling point: $\text{C}_2\text{H}_5\text{NH}_2$, $\text{C}_2\text{H}_5\text{COOH}$, $\text{C}_2\text{H}_5\text{OH}$

18. Give one test to distinguish between phenol and benzoic acid. Hr. S.B. 2018

19. Arrange the following in the order of increasing acidic strength:



20. Among $\text{C}_6\text{H}_5\text{COOH}$ and $\text{CH}_3\text{CH}_2\text{COOH}$ which is stronger acid and why? (Hr. S.B. 2018)

21. Give the IUPAC name of $\text{HOOCCH}=\text{CHCOOH}$

22. Arrange the following in the decreasing order of dipole moment:



23. Identify A and B



24. Give chemical tests to distinguish between formic acid and acetic acid. Ph. S.B. 2015

25. Write the IUPAC name of

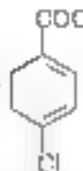



Mizoram S.B. 2014

26. Write the IUPAC name of the compound



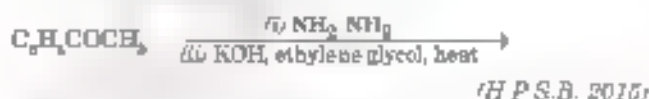
(D.S.B. 2014)

27. Among  and  which is stronger acid and why? Meghalaya S.B. 2018

28. Write the IUPAC name of $\text{CH}_3\text{CH}(\text{Cl})\text{CH}_2\text{CHO}$. (Nagaland S.B. 2015)

29. Give the IUPAC name of the following compound: $\text{CH}_2=\text{CH}-\text{CH}_2\text{CHO}$. (Assam S.B. 2015)

30. Complete the following reaction



31. Complete the following reaction: $\text{C}_6\text{H}_5\text{COCl} + \text{H}_2 \xrightarrow[\text{Quinoline or B}]{\text{Pd/BaO}_2}$ (H.P.S.B. 2015)

32. Arrange the following in the increasing order of pK_a values: CH_3COOH , ClCH_2COOH , HClCHCOOH , Cl_2CHCOOH . Assam S.B. 2018

CBSE QUESTIONS

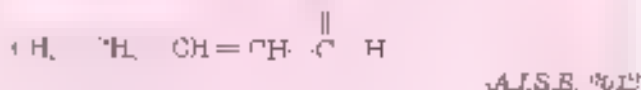
33. Write the IUPAC name of $\text{H}_2\text{C}=\text{CH}-\text{CH}=\text{CH}_2$. (A.I.S.B. 2008)

34. Write the structure of 3-pentanone. (A.I.S.B. 2009)

35. Write the structural formula of 1-phenylpropan-2-one. (A.I.S.B. 2008)

36. Write the IUPAC name of $\text{CH}_3\text{CH}(\text{CH}_3)\text{COCH}(\text{H})\text{CH}_3$. (A.I.S.B. 2010)

37. Write the IUPAC name of the following:



38. Ethanal is soluble in water. Explain. (A.I.S.B. 2013)

39. Write the structure of p-methylbenzaldehyde. (A.I.S.B. 2012)

40. Write the structure of 4-chloropentan-2-one. (A.I.S.B. 2014)

41. Write the structure of 2-hydroxybenzoic acid. (A.I.S.B. 2014)

ADDITIONAL QUESTIONS OF 1 MARK

42. The IUPAC name of the compound



- (a) 2-Oxo-but-3-enal
 (b) 3-Oxo-1-formylpent-4-enoic acid
 (c) 1-Formylpent-4-en-3-one
 (d) 3-Oxopentanoic acid

Mizoram S.B. 2017

43. Which is most acidic?

- (a) CF_3COOH (b) CCl_3COOH
(c) CBr_3COOH (d) CH_3COOH

Hr S.B. 2013

44. Among the following which has lowest pK_a value?

- (a) HCOOH (b) CH_3COOH
(c) $(\text{CH}_3)_2\text{CHCOOH}$ (d) $\text{CH}_3\text{CH}_2\text{COOH}$

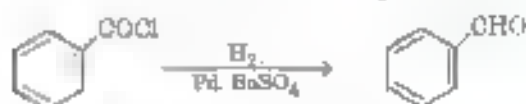
Hr S.B. 2014

45. The IUPAC name of $\text{CH}_3\text{CH}_2\text{C}(=\text{O})\text{CH}_2\text{C}(=\text{O})\text{H}$ is

- (a) 1-oxopentanal-3-one
(b) 1-oxopentanal
(c) 3-oxopentanal
(d) 3-oxopentanal-5-one

Muzoran S.B. 2015

46. What is the name of the following reaction?



- (a) Stephen reaction (b) Rosenmund reduction
(c) Retard reaction (d) Aldol condensation

Hr S.B. 2015

47. $\text{CH}_3\text{COCl} \xrightarrow[\text{BaSO}_4]{\text{Pd, H}_2} \text{X, X is}$

- (a) acetaldehyde (b) acetone
(c) ethyl chloride (d) formic acid

Hr S.B. 2015

48. Addition of HCN to a carbonyl compound is an example of

- (a) nucleophilic substitution reaction
(b) nucleophilic addition reaction
(c) electrophilic addition reaction
(d) electrophilic substitution reaction

Meghalaya S.B. 2017

49. Strongest acid is

- (a) $p\text{-ClC}_6\text{H}_4\text{COOH}$ (b) $p\text{-O}(\text{C}_2\text{H}_5)\text{COOH}$
(c) $\text{C}_6\text{H}_5\text{COOH}$ (d) $p\text{-NO}_2\text{C}_6\text{H}_4\text{COOH}$

Hr S.B. 2018

50. Strongest acid is

- (a) CH_3COOH (b) $\text{CH}_3\text{CHClCOOH}$
(c) $\text{CH}_3\text{CH}_2\text{COOH}$ (d) $\text{CH}_3\text{CH}_2\text{CH}_2\text{COOH}$

Hr S.B. 2018

51. Which on heating with aqueous KOH , produces acetaldehyde?

- (a) $\text{CH}_3\text{CH}_2\text{CH}_2\text{Cl}$ (b) CH_3COCl
(c) $\text{CH}_3\text{CH}_2\text{Cl}$ (d) $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{Cl}$

Hr S.B. 2017

52. Iodoform test is not given by

- (a) Pentan-3-one (b) Pentan-3-one
(c) Ethanol (d) Ethanal

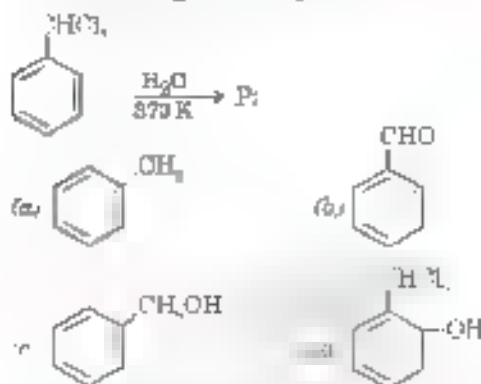
Hr S.B. 2017

53. In the following, strongest acid is

- (a) $\text{CH}_3\text{CH}_2\text{COOH}$ (b) CH_3COOH
(c) $\text{C}_6\text{H}_5\text{COOH}$ (d) $\text{C}_6\text{H}_4\text{COOH}$

Hr S.B. 2018

54. In the following reaction, product P is



Hr S.B. 2018

55. Acetaldehyde and acetone can be distinguished by

- (a) FeCl_3 test (b) NaHCO_3 test
(c) Tollen's test (d) Mohach test

Muzoran S.B. 2018

Short-Answer Questions (carrying 2 or 3 marks)

- How does $>\text{C}=\text{O}$ differ from $>\text{C}=\text{C}<$ group in chemical reactions?
- Explain the following:
 - It is necessary to control the pH during the reaction of aldehydes or ketones with ammoniacal derivatives.
 - Benzophenone does not react with sodium bisulphite.
 - Acetaldehyde gives aldol condensation while formaldehyde does not.
 - HCHO reacts with HCN faster than CH_3CHO .
 - Aldehydes and ketones undergo nucleophilic addition reactions.
- Explain the mechanism of addition of Grignard's reagent to the carbonyl group of a compound forming an adduct followed by hydrolysis. (D.S.B. 2009)
 - Illustrate the following named reaction by giving examples:
 - Cannizzaro's reaction
 - Clemmensen reduction
- Why is α -hydrogen in carbonyl compounds acidic?
 - How can you distinguish between acetophenone and benzaldehyde?
- How will you bring about the following transformations?
 - Acetic acid into acetone
 - Acetaldehyde into lactic acid
 - Acetone to iodoform
 - Propanone to propene
 - Benzene acid to *m*-nitrobenzyl alcohol

Or

Distinguish between the following pairs.

- Propanal and propanone
 - Phenol and benzoic acid
6. An organic compound $\text{P}(\text{C}_7\text{H}_6\text{O})$ reduces Tollen's reagent. On oxidation of P with acidified $\text{K}_2\text{Cr}_2\text{O}_7$, the compound A is formed which on treatment with calcium hydride forms a compound B. Dry distillation of B produces C which on warming with dilute NaOH gives D. Heating D with an acid produces E. What are A, B, C, D and E and give the reaction sequences. (Manipal S.B. 2014)

7. a. Give a chemical test with equation to distinguish between methanal and ethanal.

b. An organic compound has the molecular formula $C_5H_{10}O$. The compound does not reduce Tollen's reagent, but reacts with Brady's reagent to give orange precipitate. On vigorous oxidation, the molecule produces ethanoic acid and propanoic acid. The compound also gives iodoform test. Identify the compound and write equations for chemical reactions involved.

c. What happens when carbonyl compound is treated with zinc amalgam and concentrated hydrochloric acid? Give chemical equation. What is the name of the reaction? Assam S.B. 2018

8. a. What are Claisen-Schmidt condensation and Kolbe's reaction? Give one example of each.

b. NH_3 and its derivatives do not show nucleophilic addition reactions with aldehydes and ketones in highly acidic medium. Justify. Pb S.B. 2018

9. Write chemical reactions to affect the following transformations:

i) Butan-1-ol to butanoic acid

ii) Benzyl alcohol to phenyl ethanoic acid

iii) Benzamide to benzoic acid D.S.B. 2011

10. a. How will you convert benzoic acid to benzaldehyde?

b. How will you convert benzoic acid to ethyl benzoate?

c. Write a short note on HVZ reaction.

H.P.S.B. 2012

11. a. Boiling points of carboxylic acids are higher than the corresponding alcohols. Explain.

b. Identify compounds A to (D) in the following reactions.



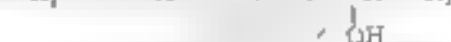
Meghalaya S.B. 2017

12. a. What are Etard reaction and Gattermann-Koch reaction? Give one example of each.

b. Aldehydes are more reactive towards nucleophilic addition reactions than ketones. Justify.

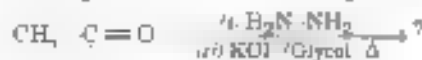
Pb. S.B. 2018

13. Name the reagents used in the following reactions:



L.S.B. 2015

14. Predict the products of the following reactions.



15. Write short notes on the following:

a) Cannizzaro's reaction

b) Rosenmund reduction

c) Friedel-Crafts acylation

Or

Give chemical tests to distinguish between the following pairs:

a. Benzoic acid and ethyl benzoate

b. Pentan-2-one and pentan-3-one

c. Benzaldehyde and acetophenone H.P.S.B. 2015

16. Write short notes on the following:

a. Aldol condensation

b. Clemmensen reduction

c. HVZ reaction

Or

Give chemical tests to distinguish between the following pairs of compounds:

a. Ethanal and propanal

b. Phenol and benzoic acid

c. Acetophenone and benzophenone H.P.S.B. 2015

17. a. Give chemical reactions for conversion of bromobenzene to benzoic acid.

b. Explain the following reactions with example:

i) Aldol condensation reaction

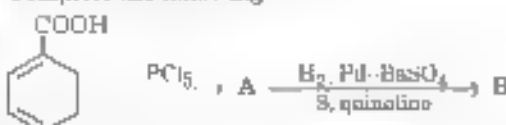
ii) Hell-Volhard-Zelinsky reaction H.P.S.B. 2015

18. a. Complete the following:



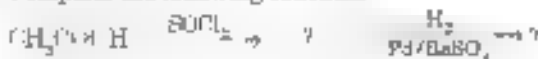
b. Aldehydes are more reactive than ketones towards nucleophilic reactions. Explain.

c. Complete the following:

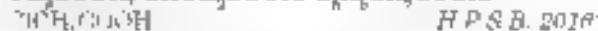


19. a. What is formalin? Pb.S.B. 2015

b. Complete the following reaction:



c. Arrange the following in increasing order of acidic strength:

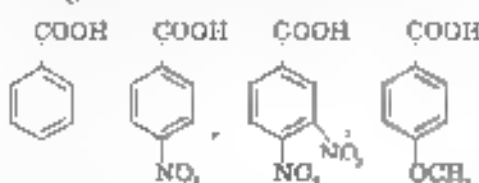


20. a. Why is the bond length of $C=O$ in carboxylic acid slightly larger than that in aldehyde and ketone?

b. Complete the following reaction:



c. Arrange the following in the order of increasing acid strength:



H.P.S.B. 2016

21. a. How will you distinguish between:



b. Complete the following reaction:



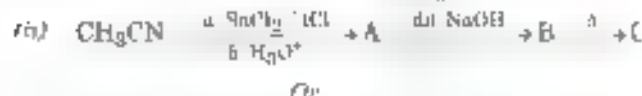
- c) Arrange the following in decreasing order of acidic strength
 H_2O , CH_3OH , $\text{C}_6\text{H}_5\text{OH}$, CH_3COOH *H.P.S.B. 2018.*
22. (a) Why are the boiling points of carboxylic acids higher than those of the corresponding alcohols?
 (b) Define the following terms and write the reaction involved in it
 i. Reimer-Tiemann reaction
 ii. Rosenmund's reduction reaction
(Nagaland S.B. 2018.)
23. Describe the following:
 (a) Wolf-Kishner reduction
 (b) Clemmensen reduction
 (c) Cross aldol condensation
Or
 Convert benzene into
 a. Benzaldehyde
 b. Benzoic acid
 c. Acetophenone *Hr S.B. 2018.*
24. (a) What is aldol-condensation reaction? Write the reaction involved in it.
 (b) What happens when
 (i) Aldehyde reacts with hydroxylamine.
 ii. Ketone reacts with hydrazine
(Nagaland S.B. 2018.)
25. (a) Why is formaldehyde more reactive than acetone?
 (b) Complete the following:
 (i) $\text{C}_6\text{H}_5\text{COOH} + \text{NH}_3 \rightarrow$
 ii. $\text{C}_6\text{H}_5\text{COOH} + \text{NaOH} \rightarrow$ *(Pb.S.B. 2018.)*
26. (a) Why are aldehydes more reactive than ketones?
 (b) Complete the following:
 (i) $\text{RCOOH} + \text{SOCl}_2 \rightarrow$
 ii. $2\text{CH}_3\text{COOH} + 2\text{Na} \rightarrow$ *Pb.S.B. 2017*
27. (a) (i) What happens when acetone reacts with H_2N ?
 ii. The melting point of butanoic acid ($\text{C}_4\text{H}_8\text{COOH}$) is higher than pentanoic acid ($\text{C}_5\text{H}_{10}\text{COOH}$). Explain.
Or
 (b) (i) What is cross-aldol condensation reaction? Give an example
 ii) what happens when acetaldehyde reacts with
 a. Hydrazine b) Phenyl hydrazine
Nagaland S.B. 2018.
28. Write short notes on the following
 (a) Reimer-Tiemann reaction *H.P.S.B. 2018*
 (b) Etard reaction
 (c) Cannizzaro reaction *H.P.S.B. 2018, Hr S.B. 2018*
Or
 (a) How will you convert methanol into ethanal?
 (b) How will you convert benzaldehyde into benzophenone?
 (c) How will you convert ethanal into ethanone? *H.P.S.B. 2017*
29. (a) How will you prepare aldehyde from
 i. Alcohol ii. RCOO_2Ca (iii) Alkyne
 (b) Why do aldehydes undergo nucleophilic addition reactions more readily than ketones? Explain
 (c) Why do carboxylic acids not give characteristic reactions of carbonyl group? *Hr S.B. 2017*
30. Explain
 i. Clemmensen's reduction
 ii) Nitration of benzaldehyde
 iii. Give reaction of HCl / H_2O with H^+CN *H.P.S.B. 2018*
31. (a) Explain Rosenmund reduction reaction with equation
 (b) How does propionyl (CH_3COCH_2) react with hydrazine? Give equation.
 (c) Name an oxidizing agent used in the Etard's reaction.
Karnataka S.B. 2018.
32. Write the following reactions
 (a) Haloforn reaction
 (b) Gattermann reaction
 (c) Hunsdiecker's reaction
 (d) Reimer-Tiemann reaction *(Pb.S.B. 2017)*
33. (i) Write Cannizzaro reaction.
 (ii) Write aldol condensation.
 (iii) Why are aliphatic carboxylic acids stronger than phenols?
Or
 (a) Carboxylic acids do not give characteristic reactions of carbonyl group. Explain.
 (b) Why do aldehydes and ketones have high dipole moment?
(Pb.S.B. 2017)
34. (i) Write Hell-Volhard-Zelinsky reaction.
 (ii) Write cross aldol condensation
 (iii) Ethanoic acid is weaker acid than benzoic acid. Why?
Pb.S.B. 2017
35. (a) Write Clemmensen reduction reaction.
 (i) Write Rosenmund reaction
 (ii) Formaldehyde give Cannizzaro reaction whereas acetaldehyde does not. Why?
Or
 (a) Aldehydes and ketones undergo a number of nucleophilic addition reactions. Why?
 (b) Acetic acid is liquid while aromatic acids are solids. Give reasons. *Pb.S.B. 2017*
36. (a) How are aldehydes distinguished from ketones using Tollen's and Fehling's reagent? Give complete chemical reactions.
 (b) A carbonyl compound with molecular weight 80, does not reduce Fehling's solution but forms crystalline bisulphite derivative and gives iodoform test. The possible compounds are
 (i) Pentan-2-one and pentan-3-one
 ii. Pentan-2-one and 3-methylbutan-2-one
 iii. Pentan-2-one and pentanal.
 (iv) Pentan-3-one and 3-methylbutan-2-one
(Manipal S.B. 2017)
37. An organic compound $\text{X}(\text{C}_3\text{H}_6\text{O})$, on oxidation, gives $\text{Y}(\text{C}_3\text{H}_4\text{O}_2)$. Compound (X) undergoes haloform reaction. On treatment with HCN , compound (X) produces Z which on hydrolysis gives 2-hydroxypropanoic acid. Identify X, Y and Z. Write the equation for the reactions involved. What happens when X is treated with dilute NaOH ? *Assam S.B. 2017*
38. (a) (i) Why are aldehydes more reactive than ketones towards nucleophilic addition reaction?
 (ii) Give the reaction involved in
 (a) Cannizzaro reaction
 (b) Clemmensen reduction
Or
 (b) (i) What is Fehling's solution test?
 (ii) Give the reaction of Grignard reagent with aldehyde and ketone. *(Nagaland S.B. 2017)*

39. Write a short note on Rosenmund's reaction giving suitable chemical reaction.

(a) Explain that the bond length of C=O in carboxylic acid is slightly larger than that in aldehydes and ketones.
Or

(b) Explain why chloroacetic acid is a stronger acid than acetic acid.
Modern S.B. 2017

40. Write structures of compounds A, B and C in each of the following reactions



Do the following conversions in not more than two steps:

(i) Benzene acid to benzaldehyde

(ii) Ethyl benzene to benzoic acid

(iii) Propanone to propene

D.S.B. 2017

41. Write the reactions involved in the following

(i) Hell-Volhard Zelinsky reaction

(ii) Decarboxylation reaction

(D.S.B. 2017)

42. Write the equations involved in the following reactions

(i) Wolff-Kishner reduction

(ii) Etard reaction

(D.S.B. 2017)

CBSE QUESTIONS

43. (a) Give chemical test to distinguish between benzaldehyde and benzoic acid.
(D.S.B. 2007)

(b) Write two chemical equations to illustrate each of the following reaction

(i) Rosenmund's reaction

(ii) Cannizzaro's reaction

(A.I.S.B. 2007)

44. Write chemical tests to distinguish between the following pairs of compounds

(i) Acetophenone and benzophenone

(ii) Ethanal and propanal

(iii) Propanal and propanone

(A.I.S.B. 2008)

45. An organic compound A contains 80.77% carbon, 11.83% hydrogen and rest oxygen. The molecular mass of the compound is 86. It does not reduce Tollen's reagent but forms an addition compound with sodium hydrogen sulphate and gives positive iodoform test. On vigorous oxidation it gives ethanoic and propanoic acids. Derive the possible structure of A.
(A.I.S.B. 2008; D.S.B. 2008, 2009)

46. Give chemical tests to distinguish between following pairs of compounds

(i) Propanal and propanone

(ii) Acetophenone and benzophenone

(iii) Phenol and benzoic acid

(A.I.S.B. 2009)

47. How will you bring about the following conversions?

(i) Ethanal to 5-hydroxybutanal

(ii) Benzaldehyde to benzophenone

(A.I.S.B. 2009)

48. (a) An organic compound A has molecular formula $\text{C}_6\text{H}_{12}\text{O}_2$. It gets hydrolysed with dil. H_2SO_4 and gives a carboxylic acid B and an alcohol C. Oxidation of C with chromic acid also produced B. C on dehydration gives but-1-ene. Write equations for the reactions involved.

(b) Write chemical equations to illustrate

Hell-Volhard-Zelinsky reaction.

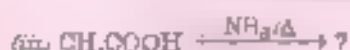
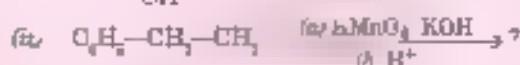
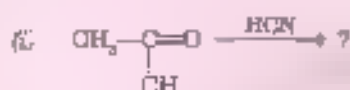
(A.I.S.B. 2009)

49. Name the reagents used in the following reactions



(A.I.S.B. 2015)

50. Predict the products of the following reactions



(A.I.S.B. 2015)

51. How do you convert the following?

(a) Ethanal to propanone

(b) Toluene to benzoic acid

Or

Answer for the following

(a) Aromatic carboxylic acids do not undergo Friedel-Crafts reactions

(b) pK_a value of 4-nitrobenzoic acid is lower than that of benzoic acid.
(A.I.S.B. 2012)

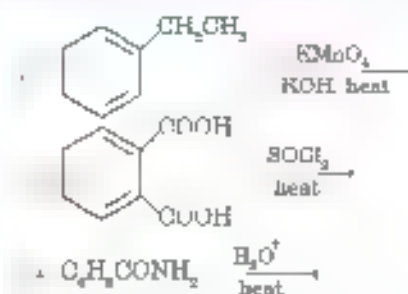
52. A, B and C are three unsyclic functional isomers of a carbonyl compound with molecular formula $\text{C}_6\text{H}_{10}\text{O}$. Isomers A and C give positive Tollen's test whereas isomer B does not give Tollen's test but gives positive iodoform test. Isomers A and B on reduction with $\text{Zn/Hg}/\text{conc. HCl}$ give the same product (D).

(a) Write the structures of A, B, C and D

(b) Out of A, B and C isomers, which one is least reactive towards addition of H^+N ?
(A.I.S.B. 2018)

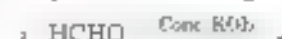
Long Answer Questions—(carrying 5 marks)

- (a) Describe the following giving linked chemical equations
(i) Cannizzaro reaction & Decarboxylation
(b) Complete the following chemical equations:



(D.S.B. 2011)

- (a) How will you bring about the following conversions?
(i) Propanone to propanal
(ii) Benzoyl chloride to benzaldehyde
(iii) Ethanal to but-2-enal
(b) Complete the following reactions

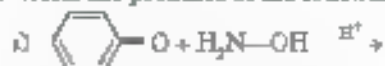


- 1c Give simple chemical tests to distinguish between the following pairs of compounds

Ethanal and Propanal

(D.S.B. 2013)

2. (a) Write the products of the following reactions.



- b) Give simple chemical tests to distinguish between the following pairs of compounds

(i) Benzaldehyde and Benzoic acid

(ii) Propanal and Propanone

Or

- 1a Account for the following

i) CH_3CHO is more reactive than CH_3COCH_3 towards reaction with HCN

- b) Write the chemical equations to illustrate the following name reactions

i. Wolff-Kishner reduction

ii. Aldol condensation

iii. Cannizzaro reaction

(D.S.B. 2014)

4. (a) Write chemical reactions to effect the following conversions

(i) Butan-1-ol to butanoic acid

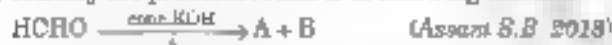
(ii) Cyclohexane to hexane-1, 5-dicarboxylic acid

(iii) Butanal to butanoic acid

(iv) Ethanoic acid to ethanoic anhydride.

(Assam S.B. 2018)

- (b) Identify the products A and B in following reaction



5. (a) An organic compound with molecular formula $\text{C}_8\text{H}_8\text{O}$ forms 2, 4-DNP derivative, reduces Tollen's reagent and undergoes Cannizzaro's reaction. On vigorous oxidation it gives 1, 2-benzenedicarboxylic acid. Identify the compound.

- (b) How will you bring about the following conversions in not more than two steps?

(i) Propanone to propene

(ii) Benzoic acid to benzaldehyde.

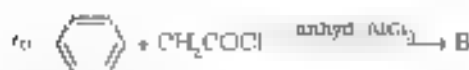
(Meghalaya S.B. 2015)

6. (a) How will you bring about the following conversions

(i) Toluene to benzaldehyde

(ii) Ethanenitrile to ethanoic acid

- (b) Identify A, B, C and D in the following reactions



(Assam S.B. 2015)

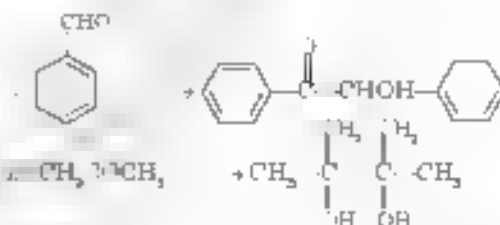
7. (a) Identify A, B, C and D in the following.



- (b) How will you convert



- (c) Write appropriate reagents for the following



- (d) Distinguish between formic acid and acetaldehyde by a suitable chemical test. (W.B. S.B. 2016)

8. (a) Arrange the following compounds in an increasing order of their reactivity in nucleophilic addition reactions

ethanal, propanal, propanone, butanone

- (b) Differentiate with chemical tests

i. Ethanal and Ethanoic acid

ii. Benzaldehyde and Acetophenone

- (c) Convert

i. Ethanal to 3-hydroxybutanoic acid

ii. Ethyl benzene to benzoic acid

Or

- (a) An organic compound having the molecular formula $\text{C}_2\text{H}_4\text{O}_3$, A, reacts with water. One molecule of (A) produces two molecules of an organic acid (B). A₂ forms an amide (C) on reaction with ammonia. (B) also forms the same amide compound. The compound (C) forms acetonitrile on reaction with P_2O_5 . Identify A, B and C. Write down the reactions.

- (b) Distinguish between the following pairs by chemical test.

$\text{C}_6\text{H}_5\text{COOH}$ and $\text{C}_6\text{H}_5\text{OH}$

- (c) Which one of the following does not respond to Tollen's test?

(a) $\text{H}_2\text{C}=\text{CHO}$

(b) CH_3CHO

(c) HCOOH

(d) CH_3COCH_3

(Tripura S.B. 2016)

9. (a) Explain why aldehydes are more reactive than ketones towards nucleophilic addition reactions

- (b) Explain with the help of chemical reactions what happens when

(i) Butan-2-one is treated with Zn/Hg and conc. HCl

(ii) two molecules of benzaldehyde are treated with conc. NaOH

(iii) acetone is treated with semicarbazide

(c) How will you differentiate between benzoic acid and phenol?

Or

(a) How will you bring about the following conversions?

- Toluene to benzaldehyde
- Benzoyl chloride to benzaldehyde
- Ethanol to propan-2-ol

(b) Arrange the following in the increasing order of their acidic strengths

- $\text{CH}_3\text{CHBrCH}_2\text{COOH}$, $\text{CH}_3\text{CH}_2\text{CHBrCOOH}$, $\text{CH}_3\text{CH}_2\text{CH}_2\text{COOH}$, $\text{BrCH}_2\text{CH}_2\text{CH}_2\text{COOH}$
- Benzoic acid, 4-nitrobenzoic acid, 2,4-dinitrobenzoic acid, 4-methoxybenzoic acid.

Meghalaya S.B. 2016.

10. Aldehydes, ketones and carboxylic acids are carbonyl compounds.

(a) Aldehydes differ from ketones in their oxidation reactions. Illustrate with one example.

(b) How will you prepare benzaldehyde by Gatterman-Koch reaction?

(c) Write the reactions of carboxylic acid with the following reagents. (Write the chemical equations)

- Thionyl chloride (SOCl_2)
- Chlorine in the presence of small amount of red phosphorus
- Lithium aluminium hydride (LiAlH_4) ether

Or

(a) Write a test to distinguish between aldehydes and ketones

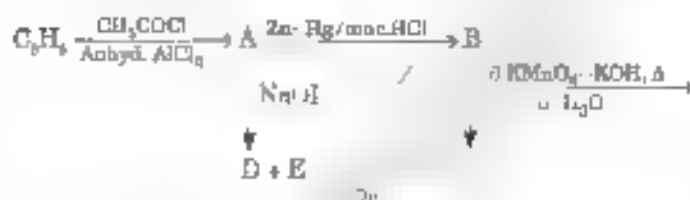
(b) How will you prepare benzaldehyde by Etard's reaction?

(c) How will you bring about the following conversions? Write the chemical equations.

- Ethanol \rightarrow ethanoic acid
- Benzamide \rightarrow benzoic acid
- Benzaldehyde \rightarrow meta nitro benzaldehyde

Kerala S.B. 2016.

11. Write the structures of A, B, C, D and E in the following reactions:

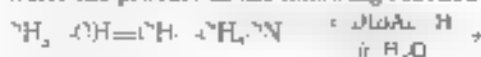


(a) Write the chemical equation for the reaction involved in Cannizzaro reaction.

(b) Draw the structure of the semicarbazone of ethanal.

(c) Why is pK_a of $\text{F-CH}_2\text{-COOH}$ lower than that of $\text{Cl-CH}_2\text{-COOH}$?

(d) Write the product in the following reaction



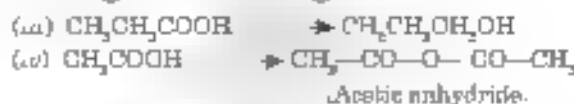
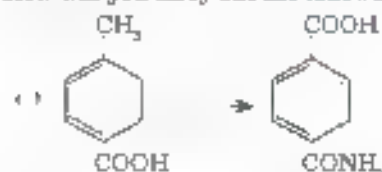
(e) How can you distinguish between propanal and propanone?

D.S.B. 2018

12. (a) The product obtained when benzene is treated with carbon monoxide and hydrogen chloride in presence of anhydrous AlCl_3 is

- Chlorobenzene
- Phenol
- Benzaldehyde
- Benzoic acid

(b) How will you carry out the following conversions?



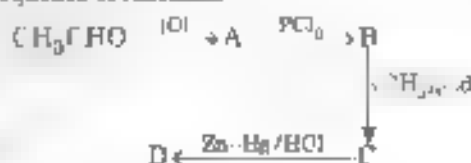
Or

Explain the following

- Esterification
- Tollen's test
- HVZ reaction
- Decarboxylation of carboxylic acid

Kerala S.B. 2017

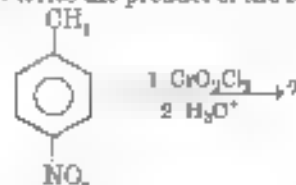
13. (a) Identify the products A, B, C and D from the following sequence of reactions



(b) Write a reaction to illustrate Cannizzaro reaction

(c) Give a simple chemical test to distinguish between benzaldehyde and acetophenone

(d) Write the product of the following reaction



Meghalaya S.B. 2017

14. (i) Give a general method of preparation of aldehyde, using a selective oxidising agent

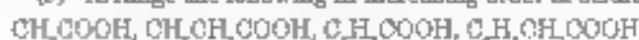
(ii) Give an example of Clemmensen reduction reaction

(iii) Identify the products A and B in the following reaction.



(iv) Write complete chemical equation for the transformation of benzamide to benzoic acid

(v) Arrange the following in increasing order of acidity



(vi) Mention one use of methanoic acid

Assam S.B. 2017

15. Write the products of the following reactions

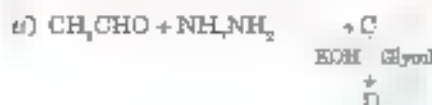


(b) Give simple chemical tests to distinguish between the following pairs of compounds

- Benzaldehyde and benzoic acid
- Propanal and propanone

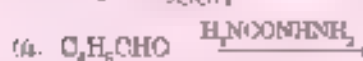
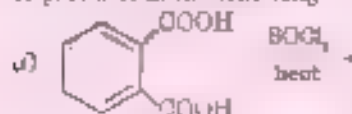
Or

- (a) Account for the following
- CH_3CHO is more reactive than CH_3COCH_3 towards reaction with HCN
 - 2-Fluorobutanoic acid is a stronger acid than 3-fluorobutanoic acid.
- b Write the chemical equations to illustrate the following name reactions
- Etard reaction.
 - Rosenmund's reaction
- c Give the mechanism of cyanohydrin formation when carboxylic anhydrides react with HCN in the presence of alkali. *CBSE Sample Paper 2017-18*
16. (a) How would you account for the following
- Aldehydes are more reactive than ketones towards nucleophilic addition reactions.
 - Boiling points of aldehydes are lower than alcohols.
 - Addition reaction of sodium hydrogen sulphite is useful for separation and purification of aldehydes.
- Kerala S.B. 2018*
- b Aromatic aldehydes undergo electrophilic substitution reactions. Write the nitration reaction of benzaldehyde with chemical equation. *Kerala S.B. 2018*
- c Write the name of products formed when salicylic acid is treated with acetic anhydride in acid medium. *Kerala S.B. 2018*
17. (a) What type of aldehydes and ketones undergo aldol condensation?
- (b) Why does benzoic acid not undergo Friedel-Crafts reaction?
- (c) Convert nitrobenzene to 3-nitrobenzoic acid.
- (d) Identify the products A, B, C and D from the following reactions

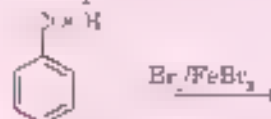
*(Meghalaya S.B. 2018)***CBSE QUESTIONS**

18. (a) Describe how the following conversions can be brought about
- Ethylbenzene to benzoic acid
 - Bromobenzene to benzoic acid
- b) Illustrate the following name reaction
Hell-Volhard-Zelinsky reaction
- c) How are the following conversions carried out
- Ethylcyanide to ethanoic acid
 - Butan-1-ol to butanoic acid
 - Methylbenzene to benzoic acid
- Write chemical equations for the involved reactions. *A.I.S.B. 2010*
19. (a) Give chemical tests to distinguish between the following
- Benzoic acid and ethyl benzoate
 - Benzaldehyde and acetophenone

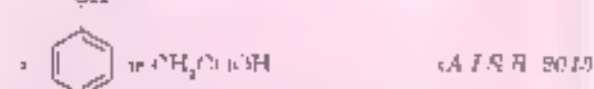
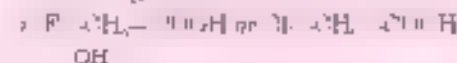
- b) Complete each synthesis by giving missing reagents or products in the following



20. (a) Illustrate the following name reactions
- Cannizzaro's reaction
 - Clemmensen reduction
- b) How would you obtain the following
- But-2-ene from ethanal
 - Butanoic acid from butanol
 - Benzoic acid from ethylbenzene *(A.I.S.B. 2011)*
21. (a) Give chemical tests to distinguish between
- Propanal and propanone
 - Benzaldehyde and acetophenone
- (b) Arrange the following compounds in an increasing order of their reactivity towards HCN : acetaldehyde, acetone, methyl tert-butyl ketone. *A.I.S.B. 2012*
22. (a) Write a suitable chemical equation to complete each of the following transformations:
- Butan-1-ol to butanoic acid
 - 4-Methylacetophenone to benzene-1,4-dicarboxylic acid
- b) Arrange the following compounds in an increasing order of their property as indicated
- Benzoic acid, 3,4-dinitrobenzoic acid, 4-methoxybenzoic acid (acid strength)
 - $\text{CH}_3\text{CH}_2\text{CH}_2\text{Br}$, COOH , $\text{CH}_3\text{CH}_2\text{Br}$, CH_3COOH , $\text{CH}_3\text{CH}_2\text{COOH}$ (acid strength). *(A.I.S.B. 2012)*
23. How will you convert the following
- Toluene to benzoic acid
 - Write products of the following reactions

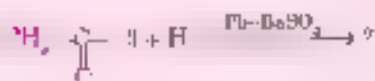
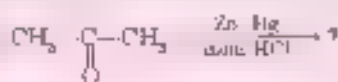


- (c) Which acid of each pair shown here would you expect to be stronger?



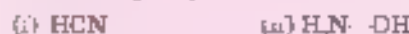
24. (a) How will you convert the following
- Propanone to Propan-2-ol
 - Ethanol to 2-hydroxypropanoic acid
- (b) Give simple chemical tests to distinguish between
- Pentan-2-one and pentan-3-one
 - Ethanal and propanal

c) Write the products of the following reactions.



A.I.S.B. 2013

26. a) Write the products formed when CH_3CHO reacts with the following reagents

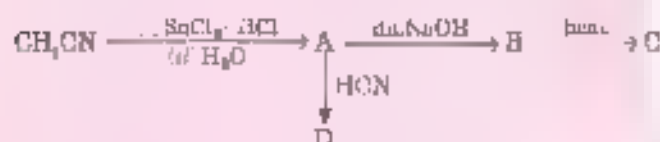


(iii) CH_3CHO in the presence of dilute NaOH

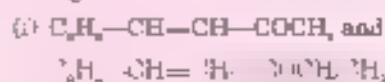
b) Give simple chemical tests to distinguish between the following pairs of compounds
Propanal and propanone

c) Out of $\text{CH}_3\text{CH}_2\text{COCH}_2\text{CH}_3$ and $\text{CH}_3\text{CH}_2\text{CH}_2\text{COCH}_3$ which gives iodoform test?
A.I.S.B. 2014

26. a) Write the structures of A, B, C and D in the following reactions



b) Distinguish between.



(ii) $\text{CH}_3\text{CH}_2\text{COOH}$ and HCOOH

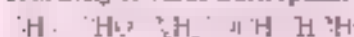
c) Arrange the following in the increasing order of their boiling points:



Or

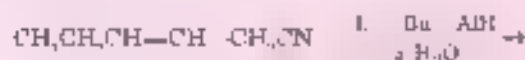
a) Write the chemical reaction involved in Etard reaction.

b) Arrange the following in the increasing order of their reactivity towards nucleophilic addition reaction



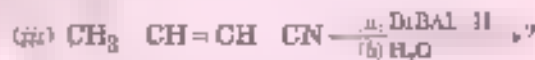
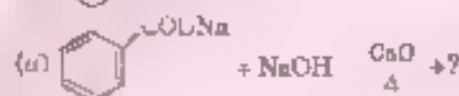
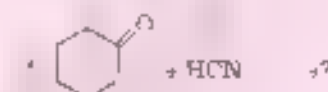
c) Why is pK_a of $\text{Cl}-\text{CH}_2-\text{COOH}$ lower than the pK_a of CH_3COOH ?

d) Write the product in the following reaction.



e) A and B are two functional isomers of compound $\text{C}_5\text{H}_8\text{O}$. On heating with NaOH and I_2 , isomer A forms yellow precipitate of iodoform; whereas isomer B does not form any precipitate. Write the formulae of A and B.
A.I.S.B. 2016

27. a) Write the products in the following reactions



b) Give simple chemical tests to distinguish between the following pairs of compounds

i) Butanal and Butan-2-one

ii) Decalin-1-one and Pinane
Or

c) Write the reactions involved in the following

i) Etard reaction

ii) Stephen reduction

d) How will you convert the following in not more than two steps

i) Benzoic acid to Benzaldehyde

ii) Acetophenone to Benzene acid

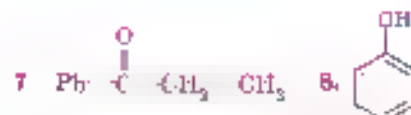
iii) Ethanoic acid to 2-Hydroxyethanoic acid
A.I.S.B. 2017

Hints & Answers

for Revision Exercises

Very Short Answer Questions

- $\text{C}_2\text{H}_5\text{COCH}_3 < \text{CH}_3\text{COCH}_3 < \text{CH}_3\text{CHO} < \text{HCHO}$
- aq° (ii) I_2/NaOH (Iodoform test)
- $(\text{CH}_3)_2\text{CCHO}$, 2, 2-Dimethylpropanal
- $\text{CH}_3\text{CH}_2\text{C}(=\text{O})\text{CH}_2\text{CH}_3$ (Pentan-3-one)
- Diphenyl methane is formed.



- butanone < propanone < propanal < ethanal
- $\text{C}_6\text{H}_5\text{COC}_2\text{H}_5 < \text{C}_6\text{H}_5\text{COCH}_3 < \text{C}_6\text{H}_5\text{CHO}$
- 4-Methylpent-3-en-2-one
- 2-Methylpropanal
- 1-Methylcyclohexanone
- $\text{CH}_3\text{CH}_2\text{CHCHO}$



15. 3-Aminobutanoal 16. 4-Hydroxypentan-2-one

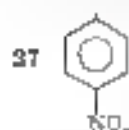
17. $\text{C}_2\text{H}_5\text{CHO} + \text{C}_2\text{H}_5\text{COCH}_3 \xrightarrow{\text{H}^+} \text{C}_4\text{H}_8\text{O} + \text{H}_2\text{O}$ 18. $\text{C}_6\text{H}_5\text{COOH}$ 20. $\text{C}_6\text{H}_5\text{COOH}$

21. But-3-enedioic acid

22. $\text{CH}_3\text{COCH}_3 > \text{CH}_3\text{CHO} > \text{CH}_3\text{COOH}$ 23. A: $\text{H}_3\text{C}(\text{OH})\text{NH}_2$ B: $\text{H}_3\text{C}(\text{OH})$

24. Propane-1, 2, 3-tricarboxylic acid

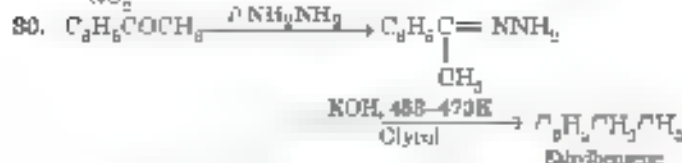
25. 3-Hydroxybutanoic acid



27.

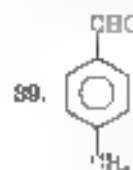
28. 3-Chlorobutanoal

29. But-3-enal

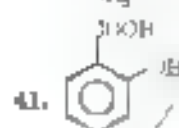
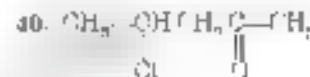
32. $\text{Cl}_3\text{CCOOH} > \text{Cl}_2\text{CHCOOH} > \text{ClCH}_2\text{COOH} > \text{CH}_3\text{COOH}$ 33. Pentan-2, 4-dione 34. $\text{CH}_3\text{CH}_2\text{C}(=\text{O})\text{CH}_2\text{CH}_3$ 

35. 2, 3-Dimethylpentan-3-one

37. Pent-2-enal



39.



41.

42. (a)

43. (a)

44. (a)

45. (c)

46. (b)

47. (a)

48. (b)

49. (d)

50. (b)

51. (a)

52. (b)

53. (c)

54. (b)

55. (c)

Competition File

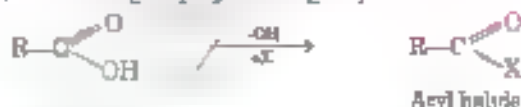
Additional Useful Information and Objective Questions

ADDITIONAL USEFUL INFORMATION

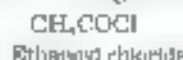
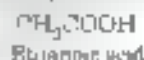
ALCOHOL DERIVATIVES: NOMENCLATURE AND METHODS OF PREPARATION AND PROPERTIES

ACYL HALIDES

These are obtained by the replacement of $-\text{OH}$ group by halide group



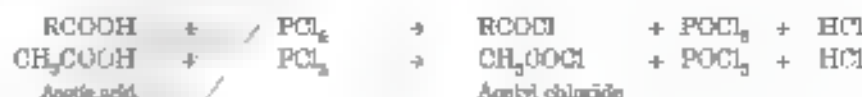
These are named by replacing the suffix $-ic$ of the name of the acid by **yl** and adding the name of the halide



Preparations

Acyl halides are easily prepared from carboxylic acids or from their salts by reaction with phosphorus pentachloride, phosphorus trichloride or thionyl chloride.

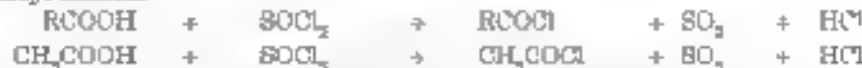
(i) With PCl_5



(ii) With PCl_3



(iii) With thionyl chloride



The reaction is best carried out with thionyl chloride because the other two products are gases

Properties

1. Hydrolysis gives acids



Competition File

2. Alcoholysis gives esters



3. Ammonolysis gives amides

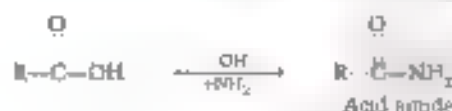


4. Reduction gives aldehydes. The reaction is called **Rosenmund's reaction**.



AMIDES

These are the compounds obtained by replacing -OH group of the carboxylic acid by -NH₂ group

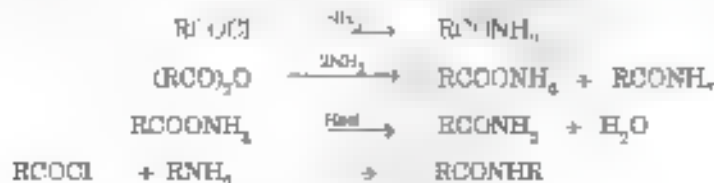


According to IUPAC system, these are named by replacing the ending -e of the parent hydrocarbon by **amide**. For example



Preparation

Amides are generally prepared by the reaction of amines or ammes with acid chlorides or acid anhydrides



Properties

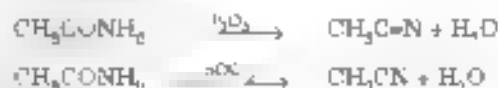
1. **Amphoteric nature.** They combine with acids as well as bases.



2. Hydrolysis



3. Dehydration



4. Action with nitrous acid

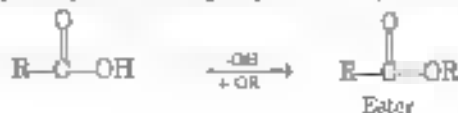


5. Action with Br₂ and caustic alkali gives amine with one carbon atom less than the amide (**Hoffmann bromamide reaction**).



ESTERS

These are obtained by replacing the -OH group of carboxylic acids by alkoxy group



Competition File

Esters are named by writing the name of alkyl or aryl group of OR part before the name of the parent acid and changing the suffix in acid to ate. For example,



Preparation

i) From carboxylic acids



The reaction is known as *esterification*.

ii) From acyl halides



iii) From acyl anhydrides



Properties

1. Hydrolysis can be done in the presence of acid as well as base



2. Ammonolysis to form amide



3. Alcoholysis (trans esterification)

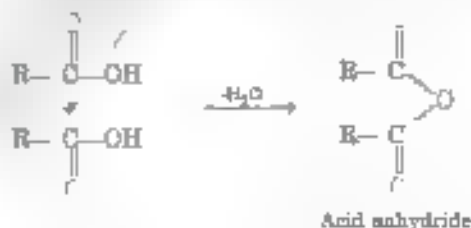


4. Reduction of esters give alcohols

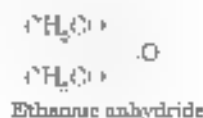


A. ID ANHYDRIDES

These are the derivative of carboxylic acids obtained by the loss of a molecule of H_2O from the carboxylic groups.



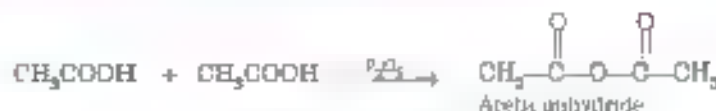
These are named as the anhydrides of the respective acids both in common and IUPAC systems. For example,



Competition File

Preparation

i) These are prepared by heating carboxylic acids with P_2O_5 .



ii) By treating sodium salt of carboxylic acid with acyl halide.

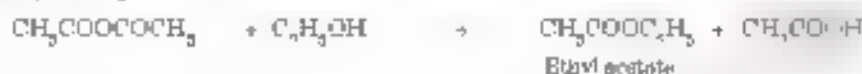


Properties

1. Hydrolysis to give acids.



2. Alcoholysis to give esters

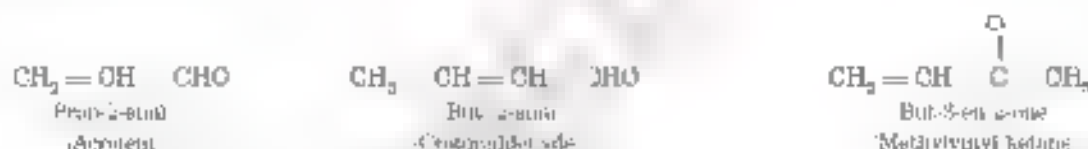


3. Ammonolysis to give amides.

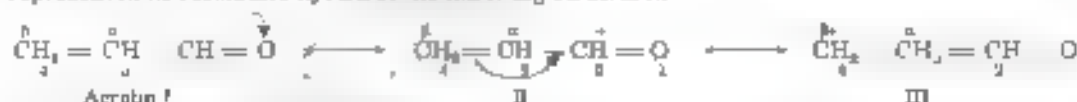


NUCLEOPHILIC ADDITION TO α, β UNSATURATED CARBONYL COMPOUNDS

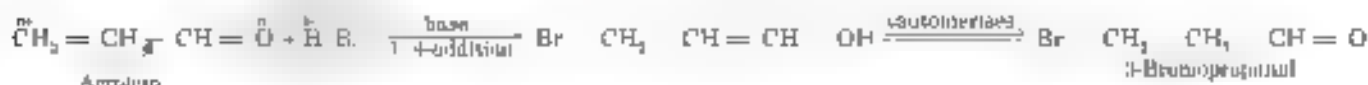
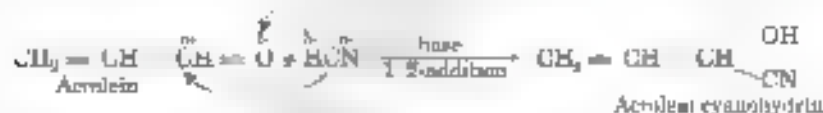
α, β unsaturated aldehydes and ketones are those compounds in which the carbonyl group is in conjugation with carbon-carbon double bond. For example,



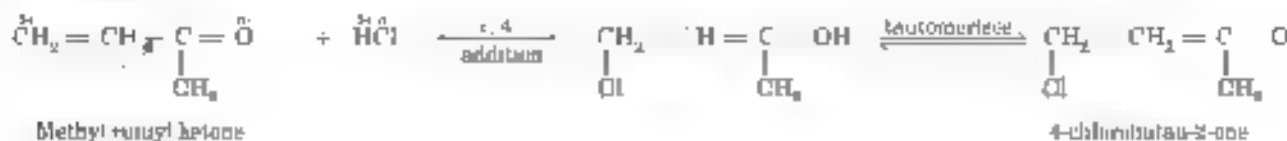
These may be represented as resonance hybrid of the following structures:



The resonance structures show that α, β unsaturated carbonyl compounds e.g. acrolein has two electron deficient sites, i.e. carbonyl carbon or C_1 carbon β to it. Therefore nucleophile may attack either at C_1 i.e. 2-addition or at C_3 i.e. 4-addition giving two different products. When the nucleophile is strong, **1, 2-addition predominates** i.e. normal addition across $C=O$ group. On the other hand if the nucleophile is weak e.g. H^+ , Br^- etc. **1, 4-addition predominates**. For example,

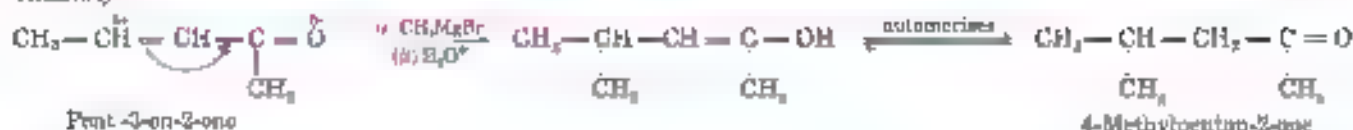


Ketones are less reactive than aldehydes and therefore, irrespective of the nature of nucleophile, **1, 4-addition product predominates**.



Competition File

Similarly



Such addition of carbanions to α, β -unsaturated compounds are commonly referred to as **Michael addition**.

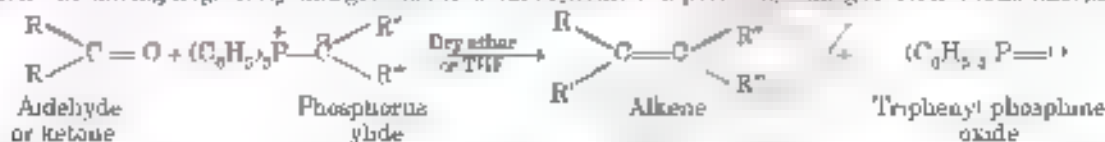
Factors governing 1,2-addition versus 1,4-addition

- Strong nucleophiles bring about 1,2-addition.
- 1,4-addition occurs readily in α, β -unsaturated ketones.
- Steric hindrance at β -position favours 1,2-addition while hindrance at the carbonyl group, favours 1,4-addition.

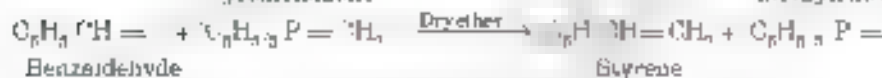
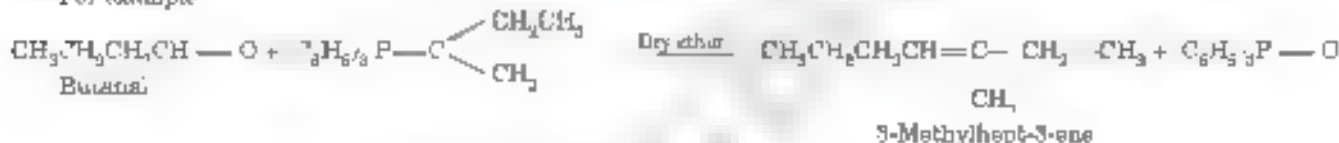
► SOME MORE IMPORTANT REACTIONS

WITTIG REACTION

Aldehydes and ketones react with phosphoranes or phosphorus ylides to give alkenes and triphenyl phosphine oxide. An ylide is a neutral molecule having negatively charged carbon atom adjacent to a positively charged heteroatom, phosphorus.



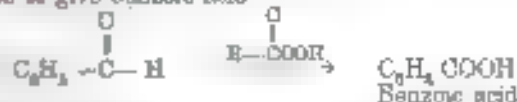
For example



It is a good method for preparing alkenes.

BAEYER VILLIGER OXIDATION OF ALDEHYDES AND KETONES

Both aldehydes and ketones are oxidised by peroxy acids. This reaction is called **Baeyer-Villiger oxidation**. For example, benzaldehyde reacts with peroxy acids to give benzoic acid.

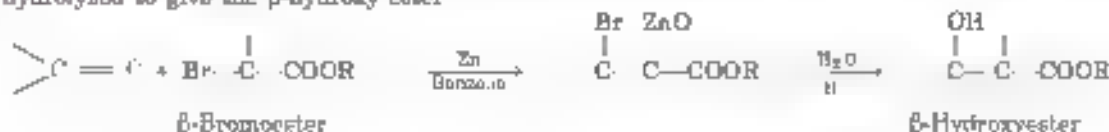


The reaction is particularly useful for ketones because it converts them to carboxylic esters. For example, acetophenone reacts with peroxy acids to give phenyl acetate.



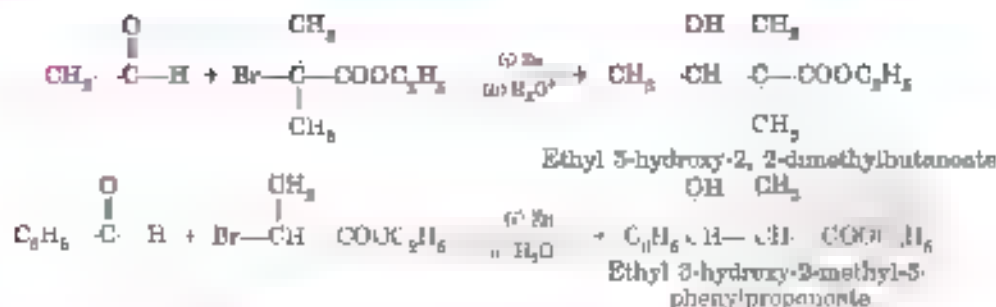
REFORMATSKY REACTION

This reaction involves the addition of an organozinc reagent to the carbonyl group of an aldehyde or ketone. The aldehyde or ketone is treated with α -bromoester in the presence of zinc metal in benzene as a solvent. The initial product is a zinc alkoxide which gets hydrolysed to give the β -hydroxy ester.



Competition File

For example,



OBJECTIVE TYPE QUESTIONS

Multiple Choice Questions

M. C. Q.

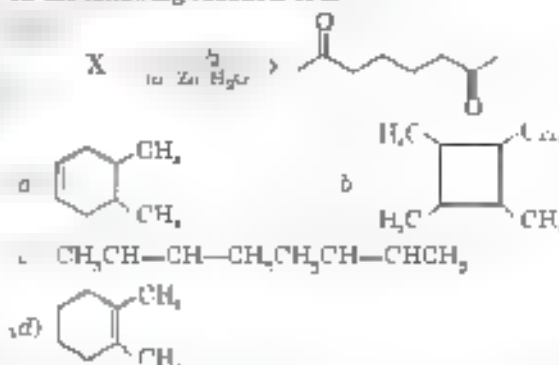
A TOPIC WISE MULTIPLE CHOICE QUESTIONS
with only one correct answer

Aldehydes & Ketones

- A1.** Benzene reacts with CH_3COCl in the presence of AlCl_3 to give
 a) $\text{C}_6\text{H}_5\text{CH}_2\text{CH}_3$ b) $\text{C}_6\text{H}_5\text{CH}_3$
 c) $\text{C}_6\text{H}_5\text{COCH}_3$ d) $\text{C}_6\text{H}_5\text{COCl}$
- A2.** Aldehydes and ketones undergo
 a) electrophilic addition b) electrophilic substitution
 c) nucleophilic addition d) nucleophilic substitution
- A3.** The molecule that can give Cannizzaro's reaction is
 a) acetaldehyde b) formaldehyde
 c) butyraldehyde d) propionaldehyde
- A4.** Which of the following is most reactive towards nucleophilic addition reactions?
 a) CH_3COCH_3 b) CH_3CHO
 c) $\text{CH}_3\text{COC}_2\text{H}_5$ d) HCHO
- A5.** In the carbonyl group, the carbon atom undergoes
 a) sp hybridisation b) sp^2 hybridisation
 c) sp^3 hybridisation d) sp^3d hybridisation
- A6.** Ketones are less reactive than aldehydes because
 a) $\text{C}=\text{O}$ group is less polar in ketones
 b) of inductive effect
 c) steric hindrance to the attacking reagent
 d) none of these
- A7.** Which of the following gives iodoform test?
 a) CH_3OH b) $\text{CH}_3\text{COCH}_2\text{CH}_3$
 c) HCHO d) CH_3COOH

- A8.** Aldehydes and ketones form hydrocarbons by
 a) Clemmensen reduction b) Cannizzaro reaction
 c) Rosenmund's reduction d) Aldol condensation

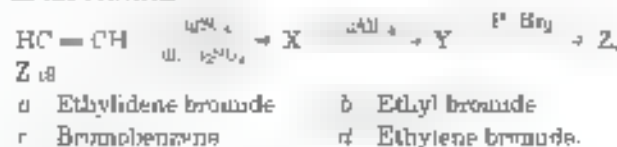
A9. In the following reaction, X is



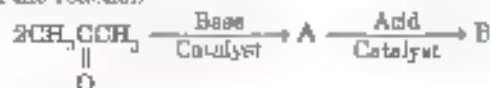
A10. Cyanohydrin of which compound gives active acid on hydrolysis?

- a) Acetaldehyde b) Formaldehyde
 c) Acetone d) Propanal

A11. In the reaction



A12. In the reaction



The product B is

- a) $\text{CH}_3\text{COCH}(\text{CH}_3)\text{CH}_2\text{COCH}_3$
 b) $\text{CH}_3\text{C}(=\text{O})\text{H} + \text{H}_2\text{C}=\text{CH}_2 + \text{H}_2\text{O}$
 c) $\text{CH}_3\text{C}(\text{CH}_3)=\text{CHCOCH}_3$
 d) $\text{CH}_3\text{CH}=\text{CHCH}_2\text{COCH}_3$

Competition File

A28. Cyanohydrin of which compound gives lactic acid on hydrolysis?

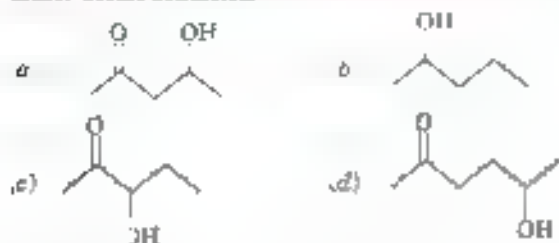
- a) Acetaldehyde (b) Formaldehyde
c) Propanal (d) Acetone

A29. An acid chloride on reaction with H_2 , Pd-BaSO₄ gives CH_3CH_2CHCHO . This acid chloride on reaction with dimethyl cadmate in the presence of dry ether, gives

- a) $(CH_3)_3COH$ (b) $(CH_3)_3CHOH$
c) $CH_3CH_2CHCOCH_3$ (d) $(CH_3)_2CHCHO$

Carboxylic Acids

A30. Which of the following will be most readily dehydrated under acidic condition?



A31. Which of the following is the strongest acid?

- a) CH_3COOH (b) $CH_3CHClCOOH$
c) CH_3CH_2COOH (d) $CH_3CH_2CH_2COOH$

A32. Acetic acid is reduced with $LiAlH_4$ to give

- a) CH_3CH_2OH (b) CH_3CHO
c) CH_3CH_3 (d) CH_3OH

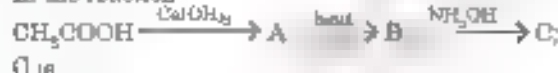
A33. Benzoic acid on treatment with HNO_3 in the presence of H_2SO_4 gives

- a) m-nitrobenzoic acid (b) nitrobenzene
c) o-nitrobenzoic acid (d) Benzene sulphonic acid

A34. Benzoic acid reacts with $LiAlH_4$ to give

- a) Ethylbenzene (b) Methylbenzene
c) Phenol (d) Benzyl alcohol

A35. In the reaction



- a) CH_3COONH_4 (b) $CH_3CH_2C=NOH$
c) $(CH_3)_2C=NOH$ (d) CH_3CONH_2

A36. Decarboxylation of sodium benzoate on heating with soda lime gives

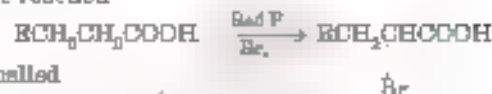
- a) benzene (b) toluene
c) benzaldehyde (d) benzoic acid

A37. The reaction



- (a) Hunsdiecker reaction
(b) Kolbe's reaction
(c) Friedel-Crafts reaction
(d) Wurtz reaction

A38. The reaction



- (a) Reimer-Tiemann reaction
(b) H₂ Volhard-Zelinsky reaction
(c) Cannizzaro's reaction
(d) Sandmeyer's reaction

A39. Vinegar is dilute aqueous solution of

- (a) Ethanoic acid (b) Benzoic acid
(c) Citric acid (d) Oxalic acid

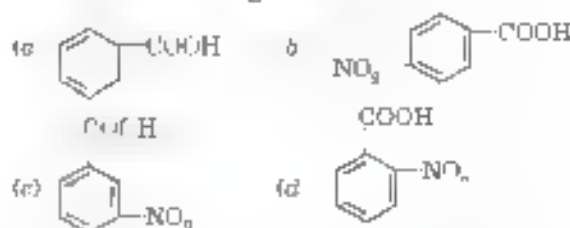
A40. The conversion of a carboxylic acid to α-bromocarboxylic acid using red phosphorus and bromine is a

- (a) Cannizzaro's reaction
(b) Aldol condensation
(c) H₂ Volhard-Zelinsky reaction
(d) Kolbe's reaction

A41. Salicylic acid on heating with soda lime ($CaO + NaOH$) gives

- (a) benzene (b) benzoic acid
(c) phenol (d) toluene

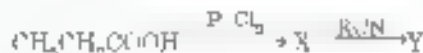
A42. Which of the following is weakest acid?



A43. The strongest acid among the following is

- (a) p-Cl-C₆H₄COOH (b) p-OHC₆H₄COOH
(c) C₆H₅COOH (d) p-NO₂C₆H₄COOH

A44. In the reaction

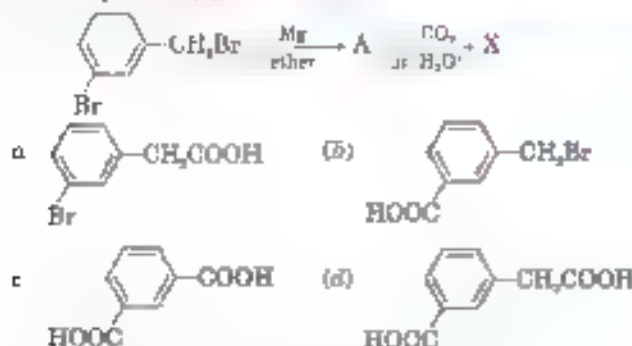


Y is

- (a) $CH_3CH_2CONH_2$
(b) $CH_3CH_2CONHCOOH$
(c) $CH_3(CN)CH_2COOH$
(d) $CH_3(CN)COOH$

Competition File

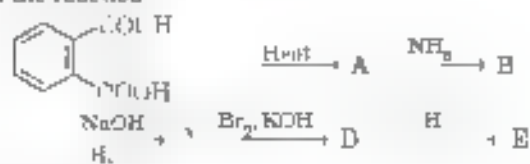
A45. The end product (D) of the reaction is



A46. Carboxylic acids are reduced by red P and HI to

- a) alkanes b) alcohols
c) alkenes d) aldehydes

A47. In the reaction



The product E is

- a) salicylic acid b) o-nitrobenzoic acid
c) anthranilic acid d) o-tolonic acid

A48. Which of the following has highest boiling point?

- a) CH_3COCl b) $(\text{CH}_3\text{CO})_2\text{O}$
c) CH_3COOH d) CH_3CHO

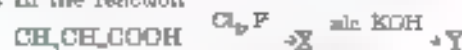
A49. Which of the following ester does not undergo Claisen self condensation?

- a) $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{COOC}_2\text{H}_5$
b) $\text{C}_6\text{H}_5\text{COOC}_2\text{H}_5$
c) $\text{C}_6\text{H}_{11}\text{CH}_2\text{COOC}_2\text{H}_5$
d) $\text{C}_6\text{H}_5\text{CH}_2\text{COOC}_2\text{H}_5$

A50. Which of the following compounds does not have a carboxyl group?

- a) Benzoic acid b) Palmitic acid
c) Picric acid d) Oleic acid

A51. In the reaction



Y is

- a) $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$
b) $\text{CH}_2=\text{CHCOOH}$
c) $\text{CH}_3\text{CH}_2\text{CN}$
d) $\text{CH}_3\text{C}(\text{Cl})=\text{COOH}$

A52. Formic acid and acetic acid can be distinguished by

- a) atomic solution b) caustic soda
c) NaHCO_3 / d) ammoniacal AgNO_3

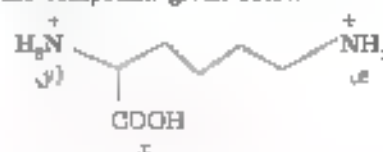
A53. The product as a result of reaction of CH_3MgBr and CO_2 on further hydrolysis gives

- a) CH_3COOH b) HCOOH
c) Oxalic acid d) Benzoic acid

A54. Which of the following will not undergo Hell Volhard Zelenko reaction?

- a) Propanoic acid
b) 2,2-dimethylpropanoic acid
c) 3-Methylpropanoic acid
d) Butanoic acid

A55. In the compound given below



The correct order of acidity of the position x, y and z is

- a) $z > x > y$ b) $x > y > z$
c) $x > z > y$ d) $y > x > z$

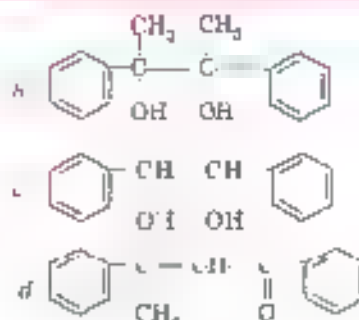
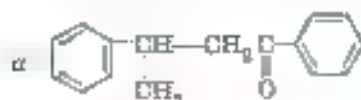
A45. d) A46. a) A47. c) A48. c) A49. b) A50. c) A51. b) A52. d) A53. a) A54. b) A55. b

B

MULTIPLE CHOICE QUESTIONS from competitive Examinations

AIJMT & Other State Boards'
Medical Entrance

B1. Acetophenone when reacted with a base, $\text{C}_6\text{H}_5\text{ONa}$, yields a stable compound which has the structure



(B.S.E. PMT 2008)

B1. d)

Competition File

B2. The relative reactivities of acyl compounds towards nucleophilic substitution are in the order of

- Ester > Acyl chloride > Amide > Acid anhydride
- Acid anhydride > Amide > Ester > Acyl chloride
- Acyl chloride > Ester > Acid anhydride > Amide
- Acyl chloride > Acid anhydride > Ester > Amide

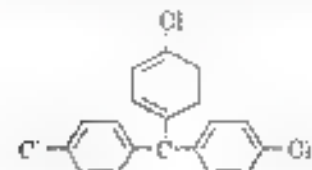
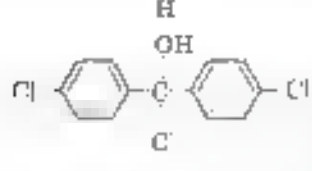
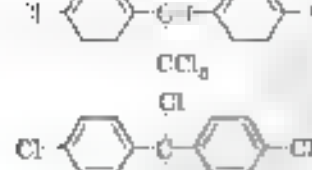
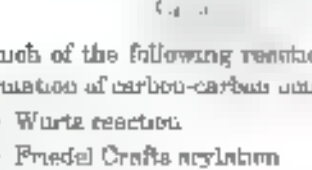
(C.B.S.E. PMT 2008)

B3. Propionic acid with Br_2/P yields a dibromo product. Its structure will be

- a) $\text{H}-\overset{\text{Br}}{\underset{\text{Br}}{\text{C}}}-\text{CH}_2\text{COOH}$ b) $(\text{H}_2\text{Br}-\text{CH}_2\text{COBr})$
- c) $\text{CH}_3-\overset{\text{Br}}{\underset{\text{Br}}{\text{C}}}-\text{COOH}$ d) $\text{CH}_2\text{Br}-\text{CH}(\text{Br})-\text{COOH}$

(C.B.S.E. PMT 2009)

B4. Trichloroacetaldehyde CCl_3CHO reacts with chlorobenzene in the presence of sulphuric acid and produces

- a) 
- b) 
- c) 
- d) 

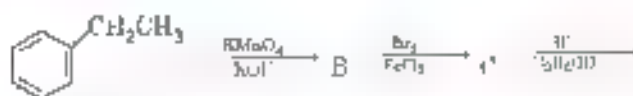
(C.B.S.E. PMT 2000)

B5. Which of the following reactions will not result in the formation of carbon-carbon bond?

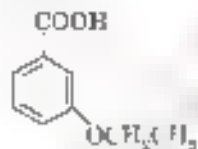
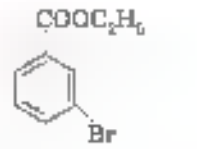
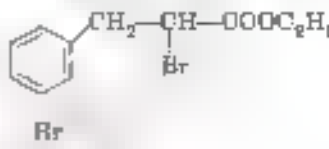
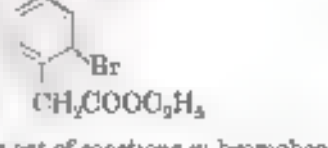
- Wurtz reaction
- Friedel Crafts acylation
- Reimer Tiemann reaction
- Canizzaro reaction

(C.B.S.E. PMT 2011)

B6. In a set of reactions, ethyl benzene yielded a product D

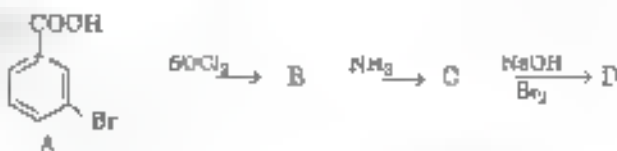


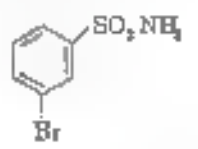
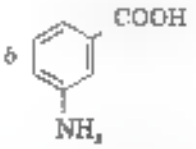
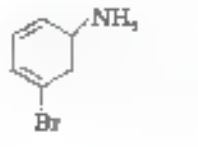
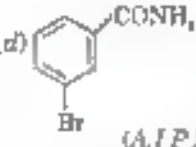
L would be

- a)  b) 
- c)  d) 

(C.B.S.E. Med 2010)

B7. In a set of reactions m-bromobenzoic acid gave a product D. Identify the product D.



- a)  b) 
- c)  d) 

(A.I.P.M.T. 2011)

B8. Clemmensen reduction of a ketone is carried out in the presence of which of the following?

- Glycol with KOH
- Zn-Hg with HCl
- LiAlH_4
- H_2 and Pt as catalyst

(A.I.P.M.T. 2011)

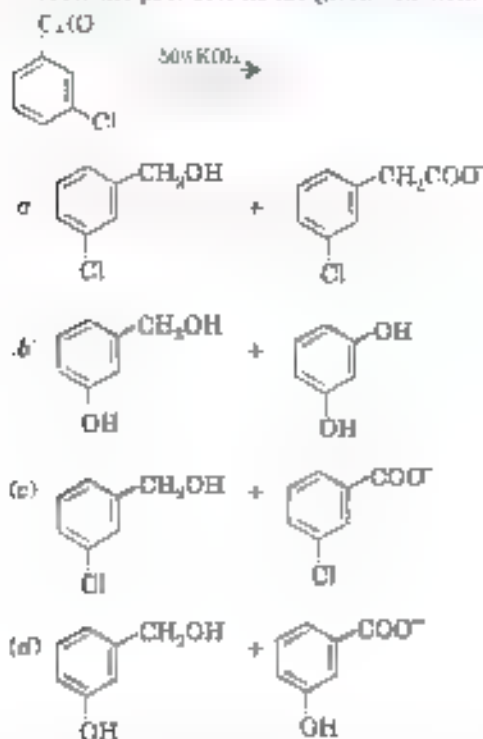
B9. CH_3CHO and $\text{C}_6\text{H}_5\text{CH}_2\text{CHO}$ can be distinguished chemically by

- Barfoed's test
- Tollens' test
- Tollen's reagent test
- Fehling's solution test

(A.I.P.M.T. 2012)

Competition File

B10. Predict the products in the given reaction.



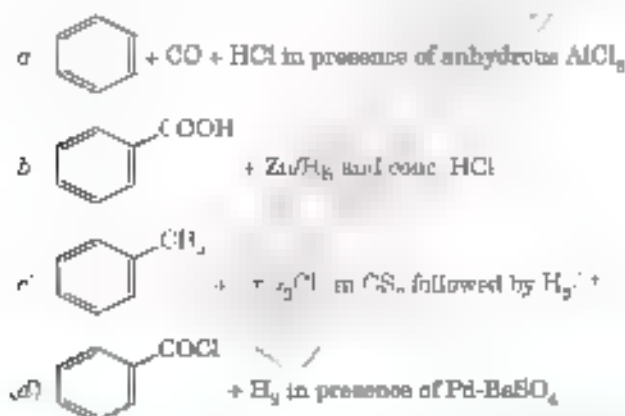
(AIPMT 2012)

B11 The correct order of decreasing acid strength of trichloroacetic acid (A), trifluoroacetic acid (B), acetic acid (C) and formic acid (D) is

- (a) $B > A > D > C$ (b) $B > D > C > A$
 (c) $A > B > C > D$ (d) $A > C > B > D$

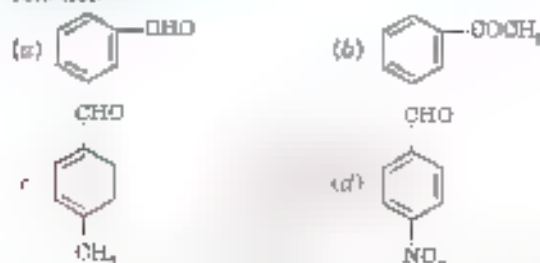
(AIPMT 2012)

B12. Reaction by which benzaldehyde cannot be prepared



NEET 2015

B13. Which one is most reactive towards nucleophilic addition reaction?



(AIPMT 2014)

B14. Which of the following will not be soluble in sodium hydrogen carbonate?

- (a) 4,4-Tetrachlorophenol
 (b) Benzoic acid
 (c) o-Nitrophenol
 (d) Benzenesulphonic acid

(AIPMT 2014)

B15. Reaction of a carbonyl compound with one of the following reagents involves nucleophilic addition followed by elimination of water. The reagent is

- (a) hydrocyanic acid
 (b) sodium hydrogen sulphate
 (c) a Grignard reagent
 (d) hydrazine in presence of feebly acidic solution

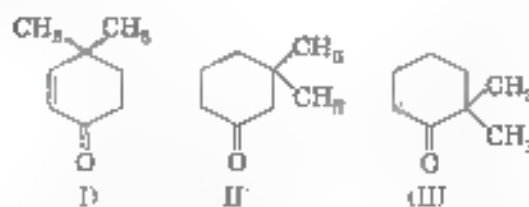
(AIPMT 2015)

B16. An organic compound 'X' having molecular formula $\text{C}_5\text{H}_{10}\text{O}$ yields phenylhydrazone and gives negative response to the iodoform test and Tollens test. It produces n-pentane on reduction. 'X' could be

- (a) pentan-3-one (b) n-amyl alcohol
 (c) pentanal (d) pentan-2-one

(AIPMT 2015)

B17 Given



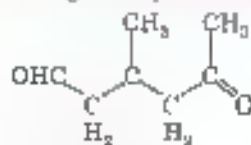
Which of the given compounds can exhibit tautomerism?

- (a) II and III (b) I, II and III
 (c) I and II (d) I and III

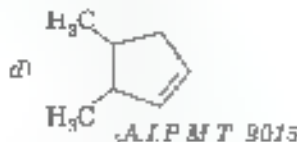
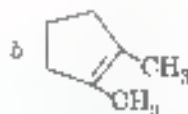
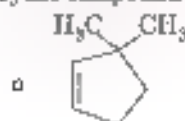
(AIPMT 2016)

Competition File

B18. A single compound of the structure



is obtainable from ozonolysis of which of the following cyclic compound?



B19. Treatment of cyclopentanone with methyl

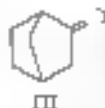
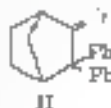


lithium gives which of the following species?

- (a) Cyclopentanonyl radical
(b) Cyclopentanonyl biradical
(c) Cyclopentanonyl anion
(d) Cyclopentanonyl cation

A.P.M.T. 2015

B20. Which among the given molecules can exhibit tautomerism?



- (a) III only
(b) Both I and III
(c) Both I and II
(d) Both II and III

(NEET 2018)

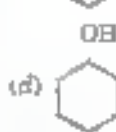
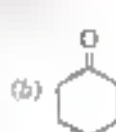
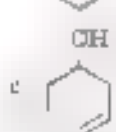
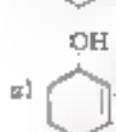
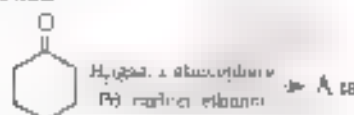
B21. The correct statement regarding a carbonyl compound with a hydrogen atom on its alpha-carbon, is

- (a) a carbonyl compound with a hydrogen atom on its alpha-carbon rapidly equilibrates with its corresponding enol and this process is known as carbonylation
(b) a carbonyl compound with a hydrogen atom on its alpha-carbon rapidly equilibrates with its corresponding enol and this process is known as keto-enol tautomerism
(c) a carbonyl compound with a hydrogen atom on its alpha-carbon never equilibrates with its corresponding enol
(d) a carbonyl compound with a hydrogen atom on its alpha-carbon rapidly equilibrates with its corresponding enol and this process is known as aldehyde-ketone equilibration. (NEET 2018)

B22. The product formed by the reaction of an aldehyde with a primary amine is

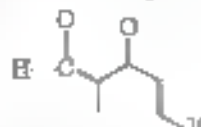
- (a) carboxylic acid
(b) aromatic acid
(c) Schiff's base
(d) ketone (NEET 2016)

B23. The correct structure of the product A formed in the reaction



(NEET 2016)

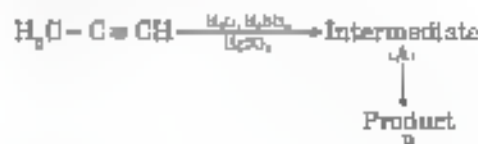
B24. The IUPAC name of the compound



- (a) 2-formylhex-2-en-5-one
(b) 5-methyl-4-naphthol-2-en-6-ol
(c) 3-keto-2-methylhex-5-enal
(d) 3-keto-2-methylhex-4-enal

(NEET 2017)

B25. Predict the correct intermediate and product in the following reaction

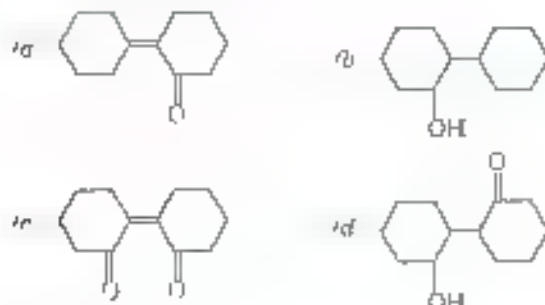


- (a) A $\text{H}_3\text{C}-\text{C}(\text{OH})=\text{CH}_2$ B $\text{H}_3\text{C}-\text{C}(\text{SO}_3\text{H})=\text{CH}_2$
b A $\text{H}_3\text{C}-\text{C}(\text{OH})-\text{CH}_3$ B $\text{H}_3\text{C}-\text{C}=\text{CH}_2$
c A $\text{H}_3\text{C}-\text{C}(\text{OH})-\text{CH}_3$ B $\text{H}_3\text{C}-\text{C}(\text{SO}_3\text{H})-\text{CH}_3$
d A $\text{H}_3\text{C}-\text{C}(\text{SO}_3\text{H})=\text{CH}_2$ B $\text{H}_3\text{C}-\text{C}(\text{SO}_3\text{H})-\text{CH}_3$

(NEET 2017)

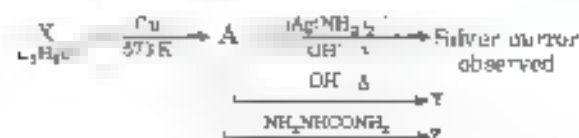
Competition File

B26. Of the following which is the product formed when cyclohexanone undergoes aldol condensation followed by heating?



NEET 2017

B27. Consider the reactions

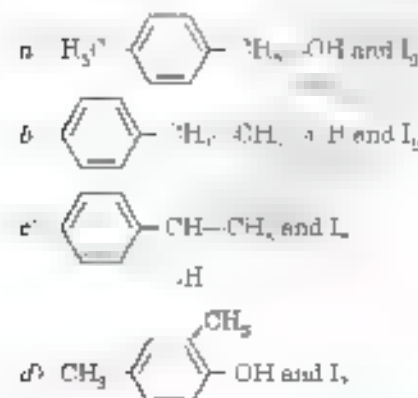


Identify A, X, Y and Z

- (a) A-Methoxymethane, X-Ethanol, Y-Ethanoic acid, Z-Semicarbazide
 (b) A-Ethanol, X-Ethanol, Y-But-2-enal, Z-Semicarbazone
 (c) A-Ethanol, X-Acetaldehyde, Y-Butanone, Z-Hydrazine
 (d) A-Methoxymethane, X-Ethanoic acid, Y-Acetate ion, Z-Hydrazine.

NEET 2017

B28. Compound A, $\text{C}_6\text{H}_5\text{O}$, is found to react with NaO_2 (produced by reacting Y with NaOH) and yields a yellow precipitate with characteristic smell. A and Y are respectively



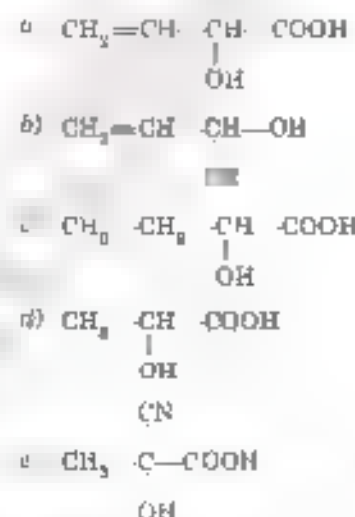
NEET 2018

B29. Carboxylic acids have higher boiling points than aldehydes, ketones and even alcohols of comparable molecular mass. It is due to their

- (a) formation of intramolecular H-bonding
 (b) formation of carboxylate ion
 (c) more extensive association of carboxylic acid via van der Waals forces of attraction
 (d) formation of intermolecular H-bonding.

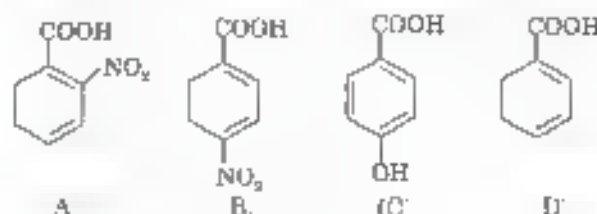
NEET 2018

B30. $\text{CH}_3\text{CHO} + \text{HCHO} \xrightarrow[\text{Heat}]{\text{dil. NaOH}} \text{A} \xrightarrow[\text{H}_2\text{O}]{\text{HCN}} \text{B}$ the structure of compound B is



Kerala P M T 2005

B31. Arrange the following acids in order of their increasing acidity

(a) $\text{A} < \text{B} < \text{C} < \text{D}$ (b) $\text{B} < \text{C} < \text{A} < \text{D}$ (c) $\text{C} < \text{B} < \text{D} < \text{A}$ (d) $\text{D} < \text{C} < \text{B} < \text{A}$

A.M.U. 2011

B32. 5-oxohexanal is obtained by ozonolysis of



A.M.L. Med 2013

Competition File

B30. Which of the following carboxylic acid undergoes decarboxylation easily?

- a) $C_6H_5COCH_2COOH$ (b) $C_6H_5CHCOOH$

- c) $C_6H_5CHCOOH$ (d) $C_6H_5COCOCH_3$

NH

A.M.U. Med 2013

B34. When a mixture of benzaldehyde and acetophenone is treated with dilute NaOH at 298 K, it forms

- (a) 2,3-diphenylpropanal
(b) 1,1-diphenylpropan-2-one
(c) 1,3-diphenylprop-2-en-1-one
(d) 1,2-diphenylprop-2-en-1-one
(e) 1,3-diphenylprop-2-en-1-one

Kerala PMT 2015

JEE (Main) & Other State Boards' Engineering Entrance

B35. In the following sequence of reactions, the alkene affords the compound 'B'



The compound B is

- (a) CH_3CHO (b) CH_3CH_2CHO
(c) CH_3COCH_3 (d) $CH_3CH_2COCH_3$

A.I.E.E.E. 2008

B36. One mole of a symmetrical alkene on ozonolysis gives two moles of an aldehyde having molecular mass of 44. The alkene is

- (a) But-2-ene (b) Ethene
(c) Propene (d) But-1-ene

A.I.E.E.E. 2010

B37. The correct order of increasing basicity of the given conjugate bases ($R = CH_3$) is

- (a) $RCOO^- < NH_2^- < HC \equiv C^- < R^-$
(b) $RCOO^- < HC \equiv C^- < NH_2^- < R^-$
(c) $RCOO^- < HC \equiv C^- < R^- < NH_2^-$
(d) $R^- < HC \equiv C^- < RCOO^- < NH_2^-$ (A.I.E.E.E. 2010)

B38. Which of the following reagents may be used to distinguish between phenol and benzoic acid?

- (a) Aqueous NaOH (b) Tollen's reagent
(c) Molisch reagent (d) Neutral $FeCl_3$

A.I.E.E.E. 2011

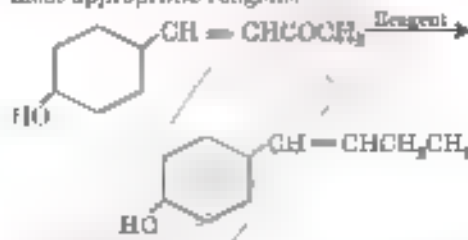
B39. Trichloroacetaldehyde was subjected to Cannizzaro's reaction by using NaOH. The mixture of the products contains sodium trichloroacetate ion and another

compound. The other compound is

- (a) 2,2,2-trichloroethanol
(b) trichloromethanol
(c) 2,2,2-trichloropropanol
(d) chloroform

A.I.E.E.E. 2011

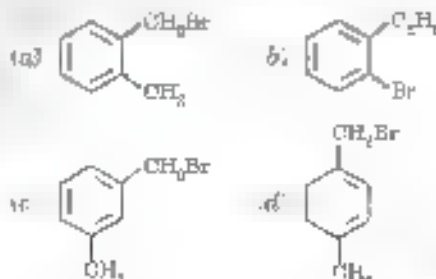
B40. In the given transformation, which of the following is the most appropriate reagent?



- (a) $Zn-Hg/HCl$ (b) $Na, liq. NH_3$
(c) $NaBH_4$ (d) NH_2-NH_2/OH

A.I.E.E.E. 2013

B41. Compound A, C_8H_9Br , gives a light yellow precipitate when warmed with alcoholic $AgNO_3$. Oxidation of A gives an acid B, $C_8H_6O_4$. (B) easily forms anhydride on heating. Identify the compound A



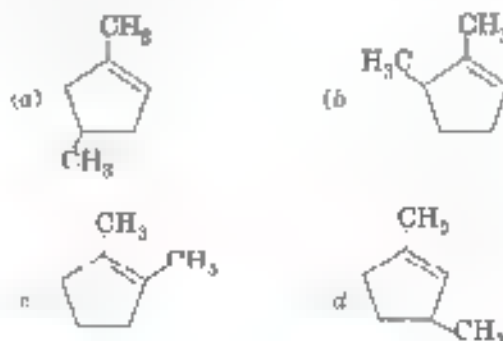
JEE Main 2013

B42. In the reaction



- (a) acetyl chloride (b) acetaldehyde
(c) acetylene (d) ethylene (JEE Main 2014)

B43. Which compound would give 5-keto-2-methyl-hexanal upon ozonolysis?



JEE Main 2015

Competition File

B44. In the following sequence of reactions

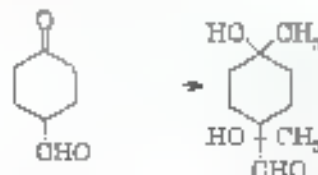


the product (C) is

- (a) $\text{C}_6\text{H}_5\text{CH}_2\text{OH}$ (b) $\text{C}_6\text{H}_5\text{CH}_3$
(c) $\text{C}_6\text{H}_5\text{COOH}$ (d) $\text{C}_6\text{H}_5\text{CH}_3$

(JEE Main 2014)

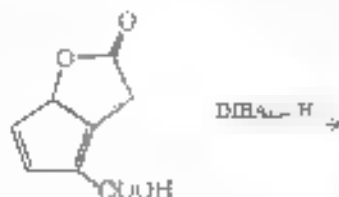
B45. The correct sequence of reagents for the following conversion will be



- (a) $\text{Ag}(\text{NH}_3)_2^+ \text{OH}^-$, $\text{H}^+/\text{CH}_3\text{OH}$, CH_3MgBr
(b) CH_3MgBr , $\text{H}^+/\text{CH}_3\text{OH}$, $\text{Ag}(\text{NH}_3)_2^+ \text{OH}^-$
(c) CH_3MgBr , $\text{Ag}(\text{NH}_3)_2^+ \text{OH}^-$, $\text{H}^+/\text{CH}_3\text{OH}$
(d) $\text{Ag}(\text{NH}_3)_2^+ \text{OH}^-$, CH_3MgBr , $\text{H}^+/\text{CH}_3\text{OH}$

(JEE Main 2017)

B46. The major product obtained in the following reaction is



- (a) (b)
(c) (d)

(JEE Main 2017)

B47. Which of the following pairs can be distinguished by sodium hypochlorite?

- (a) CH_3CHO and CH_3COCH_3
(b) $\text{CH}_3\text{CH}_2\text{CHO}$ and CH_3COOH
(c) $\text{CH}_3\text{CH}_2\text{OH}$ and $\text{CH}_3\text{CH}_2\text{CHOHCH}_3$
(d) CH_3OH and $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$
(e) CH_3OH and $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$

(Kerala P.E.T 2011)

B48. The relative acidic strengths of benzoic acid, *o*-toluic acid and *p*-toluic acid is of the decreasing order
(a) *p*-toluic acid > *o*-toluic acid > benzoic acid
(b) *o*-toluic acid > *p*-toluic acid > benzoic acid
(c) *p*-toluic acid > benzoic acid > *o*-toluic acid
(d) *o*-toluic acid > benzoic acid > *p*-toluic acid

(Karnataka C.E.T 2012)

B49. Upon treatment with I_2 and aqueous NaOH , which of the following compounds will form iodoform?

- (a) $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CHO}$
(b) $\text{CH}_3\text{CH}_2\text{COCH}_2\text{CH}_3$
(c) $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$
(d) $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}(\text{OH})\text{CH}_3$

(W.B.J.E.E. 2012)

B50. Which of the following does not give Cannizzaro's reaction?

- (a) $p\text{-NO}_2\text{-C}_6\text{H}_4\text{-CHO}$ (b) $\text{C}_6\text{H}_5\text{CHO}$
(c) HCHO (d) CH_3CHO

(Odisha J.E.E. 2012)

B51. A carbonyl group can be converted into $-\text{CH}_2-$ by

- (a) $\text{NH}_2\text{NH}_2/\text{HCl}$ (b) $\text{Zn}/\text{Hg}/\text{conc. HCl}$
(c) H_2/Ni (d) LiAlH_4

(Odisha J.E.E. 2012)

B52. In the following species, the one which is likely to be the intermediate during benzoin condensation of benzaldehyde, is

- (a) (b)
(c) (d)

(W.B.J.E.E. Engg. 2013)

B53. Bromination of PhCOOMe in acetic acid medium produces mainly

- (a) (b)
(c) (d)

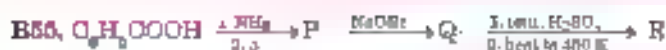
(W.B.J.E.E. Engg. 2013)

B54. The correct increasing order of the acid strength of benzoic acid (I), 4-nitrobenzoic acid (II), 3, 4-dinitrobenzoic acid (III) and 4-methoxybenzoic acid (IV) is

- (a) $\text{I} < \text{II} < \text{III} < \text{IV}$ (b) $\text{II} < \text{I} < \text{IV} < \text{III}$
(c) $\text{IV} < \text{I} < \text{II} < \text{III}$ (d) $\text{IV} < \text{II} < \text{I} < \text{III}$
(e) $\text{I} < \text{IV} < \text{II} < \text{III}$

(Kerala PET 2014)

Competition File



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- a) o-bromosulphanilic acid
b) sulphanilamide
c) sulphanilic acid
d) p-bromosulphanilamide (Karnataka CET 2014)

B56. Among the following compounds, the one(s) that gives (give) effervescence with aqueous NaHCO_3 solution is (are)

- (i) $\text{CH}_3\text{CO}_2\text{O}$ (ii) CH_3COOH
(iii) PhOH (iv) CH_3COOCHO
a) i and ii b) i and iii
c) only iii d) ii and iii (WB JEE 2014)

B57. An organic compound with the molecular formula $\text{C}_8\text{H}_8\text{O}$ forms 2, 4-DNP derivative, reduces Tollen's reagent and undergoes Cannizzaro reaction. On vigorous oxidation, it gives 1, 3-benzenedicarboxylic acid. The organic compound is

- a) 2-ethylbenzaldehyde (b) 2-methylbenzaldehyde
c) acetophenone (d) 3-methylbenzaldehyde
e) phenylacetaldehyde. (Kerala PET 2014)

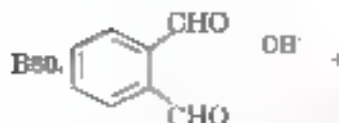
B58. Identify the combination of compounds that undergo aldol condensation followed by dehydration to produce but-2-enal

- a) Methanal and ethanol
b) Two moles of ethanol
c) Methanal and propanone
d) Ethanal and propanone
e) Two moles of ethanol (Kerala PET 2014)

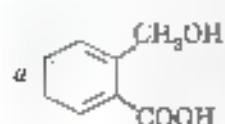
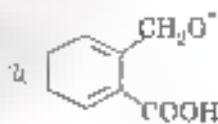
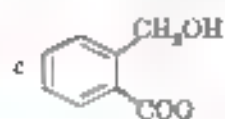
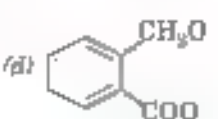


18

- (a) propanone (b) ethanone
(c) ethanenitrile (d) ethanal (Karnataka CET 2014)



the product of the above reaction is

- a)  b) 
c)  d)  (WB JEE 2015)

B61. Amongst the following compounds, the one that will not respond to Cannizzaro reaction upon treatment with alkali is

- a) $\text{C}_6\text{H}_5\text{CHO}$ b) Me_3CCHO
c) $\text{C}_6\text{H}_5\text{CHO}$ d) HCHO (WB JEE 2016)

B62. Ozonolysis of an alkene produces only one dicarbonyl compound. The structure of the alkene is

- a) $\text{CH}_3\text{—CH=CH—CH}_3$



- (d) $\text{H}_3\text{C—CH=CH—CH=CH}_2$ (WB JEE 2016)

B63. Which one of the following involves nucleophilic addition?

- a) Kolbe's reaction of phenol
b) Williamson's synthesis of ethers
c) Reimer-Tiemann reaction of phenol
d) Kolbe electrolytic synthesis of ethane from sodium acetate
e) Aldol formation from ethanal (Kerala PET 2016)

B64. An organic compound X is oxidised by using acidified $\text{K}_2\text{Cr}_2\text{O}_7$ solution. The product obtained reacts with phenylhydrazine but does not answer silver mirror test. The compound X is

- a) propan-2-ol b) ethanol
c) benzene d) $\text{CH}_3\text{CH}_2\text{CH}_3$
(Karnataka CET 2016)

B65. Predict the product 'C' in the following series of reactions.



- (b) $\text{CH}_3\text{CH(OH)C}_6\text{H}_5$

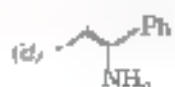
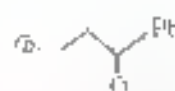
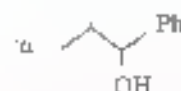
- (c) $\text{CH}_3\text{CH(OH)C}_6\text{H}_5$

- (d) $(\text{CH}_3)_2\text{C(OH)C}_6\text{H}_5$ (Karnataka CET 2016)

B66. For the reaction below



the structure of the product Q is



(WB JEE 2017)

Competition File

B67. Cannizzaro's reaction is an example of auto oxidation.

- (a) It is a typical reaction of aliphatic aldehyde.
 (b) It is a reaction answered by only aldehydes not containing α -hydrogen.
 (c) It is a reaction answered only by aromatic aldehydes.
 (d) It is a reaction answered by all aldehydes.

(Karnataka C.E.T 2017)

B68. The condensation reaction between one equivalent of acetone and two equivalents of benzaldehyde in presence of dilute alkali leads to the formation of

- (a) benzalacetophenone
 (b) benzylidenacetone
 (c) benzoin acid and acetic acid
 (d) only benzoic acid.

(Kerala P.E.T 2017)

B69. In the IUPAC system, $\text{PhCH}_2\text{CH}_2\text{CO}_2\text{H}$ is named as

- (a) 3-phenylpropanoic acid
 (b) benzylacetic acid
 (c) carboxyethyl benzene
 (d) 2-phenylpropanoic acid.

(W.B. J.E.E 2017)

B70. The correct order of acid strengths of benzoic acid (X), peroxybenzoic acid (Y) and *p*-nitrobenzoic acid (Z) is




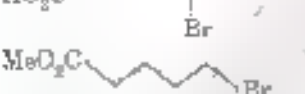
- (a) $Y > Z > X$
 (b) $Z > Y > X$
 (c) $Z > X > Y$
 (d) $Y > X > Z$.

(W.B. J.E.E. 2017)

B71. The reaction sequence given below gives product R.



The structure of the product R is

- (a) 
 (b) 
 (c) 
 (d) 

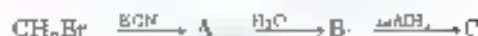
(W.B. J.E.E. 2017)

B72. Lower members of aliphatic carboxylic acid are soluble in water. This is due to

- (a) formation of hydrogen bonds with water
 (b) London forces
 (c) water is non-electrolyte
 (d) Van der-Waals interaction with water molecules.

(Karnataka C.E.T 2017)

B73. In the following sequence of reactions,



The end product C is

- (a) methane (b) ethyl alcohol
 (c) acetone (d) acetaldehyde

(Karnataka C.E.T 2017)

B74. X and Y in the below reaction are and respectively



- (a) SOCl_2 and $\text{C}_6\text{H}_5\text{CHO}$
 (b) $(\text{COCl})_2$ and $\text{C}_6\text{H}_5\text{CH}_3$
 (c) SOCl_2 and $\text{C}_6\text{H}_5\text{CH}_3$
 (d) COCl_2 and $\text{C}_6\text{H}_5\text{CH}_2\text{OH}$
 (e) SOCl_2 and $\text{C}_6\text{H}_5\text{CH}_2\text{Cl}$

(Kerala P.E.T 2017)

B75. The correct increasing order of the acid strength of acids, butyric acid (I), 3-chlorobutyric acid (II), 2-chlorobutyric acid (III), and 2,2-dichlorobutyric acid (IV) is

- (a) $I < II < III < IV$
 (b) $III < II < IV < I$
 (c) $I < III < II < IV$
 (d) $III < I < II < IV$
 (e) $IV < III < II < I$

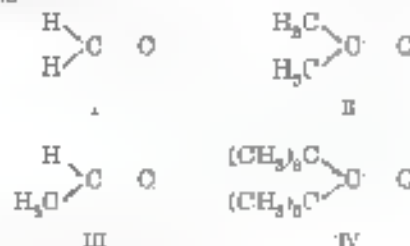
(Kerala P.E.T 2017)

B76. $\text{C}_6\text{H}_{10}\text{O} \xrightarrow[\text{H}_2\text{SO}_4]{\text{K}_2\text{Cr}_2\text{O}_7} \text{C}_6\text{H}_8\text{O} \xrightarrow[\text{warm}]{\text{LiAlH}_4/\text{NaOH}} \text{CH}_3$. Here, N is

- (a) 
 (b) 
 (c) 
 (d) 

(W.B. J.E.E 2018)

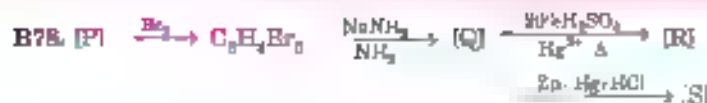
B77. The correct order of reactivity for the addition reaction of the following carbonyl compounds with ethyl magnesium iodide is



- (a) $I > III > II > IV$
 (b) $IV > III > II > I$
 (c) $I > II > IV > III$
 (d) $III > II > I > IV$

(W.B. J.E.E 2018)

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The species P, Q, R and S respectively are

- (a) ethene, ethyne, ethanal, ethane
 (b) ethane, ethyne, ethanal, ethene
 (c) ethene, ethyne, ethanal, ethanol
 (d) ethyne, ethane, ethene, ethanal (WB JEE 2018)

B79. Which of the following compound undergoes haloform reaction?

- (a) CH_3COCH_3 (b) $HCHO$
 (c) CH_3CH_2Br (d) CH_3-O-CH_3
 Karnataka CET 2018

B80. The appropriate reagent for the following transformation is



- (a) $Zn-Hg/HCl$
 (b) H_2N-NH_2 , KOH /ethylene glycol
 (c) Ni/H_2
 (d) $NaBH_4$ (Karnataka CET 2018)

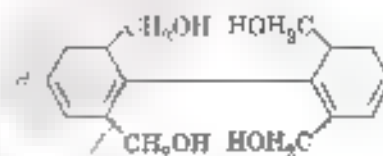
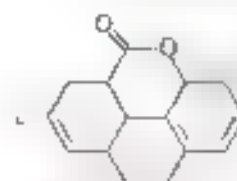
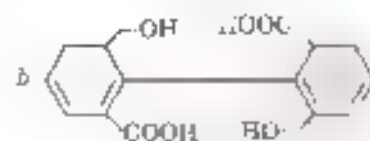
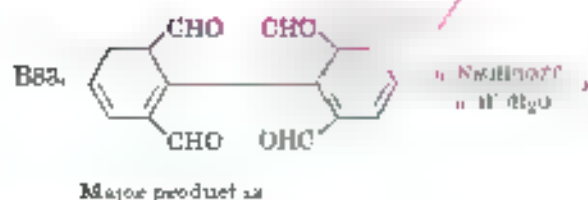
B81. The compound that does not undergo haloform reaction is

- (a) acetaldehyde (b) ethanol
 (c) acetone (d) acetophenone
 Kerala PET 2018

B82. The ease of hydrolysis in the compounds

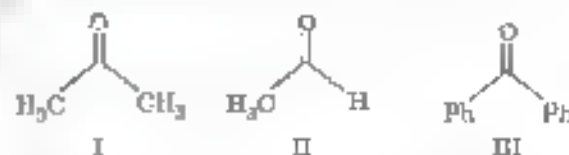
- CH_3COCl (I), CH_3COOCH_3 (II), $CH_3COOC_2H_5$ (III) and CH_3CONH_2 (IV) is of the order
 (a) $I > II > III > IV$ (b) $IV > III > II > I$
 (c) $I > II > IV > III$ (d) $I > IV > III > II$
 WB JEE 2018

JEE Advance for IIT Entrance



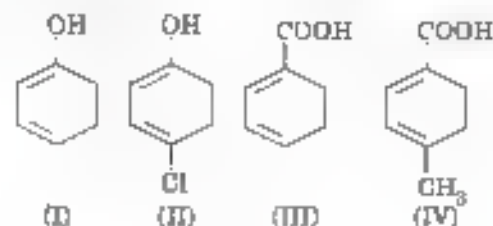
IIT 2003

B84. The order of reactivity of phenyl magnesium bromide with the following compounds is



- (a) $I > III > II$ (b) $I > III > II$
 (c) $II > I > III$ (d) All react with same rate
 IIT 2004

B85. The correct acidity order of the following is

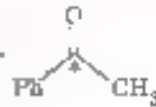
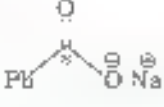
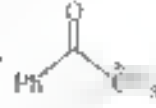
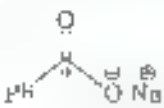
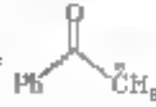
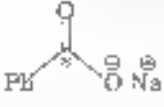
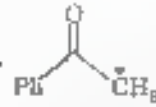
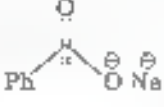


- (a) $III > IV > II > I$ (b) $IV > III > I > II$
 (c) $III > II > I > IV$ (d) $II > III > IV > I$
 IIT 2007

Competition File

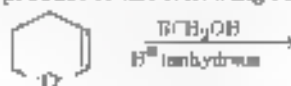
- B86.** In the following reaction sequence, the correct structures of E, F and G are



- (a) E =  F =  G = CH_3I
- (b) E =  F =  G = CH_3I
- (c) E =  F =  G = ^3HI
- (d) E =  F =  G = $^3\text{CH}_3\text{I}$

IIT 2008

- B87.** The major product of the following reaction is

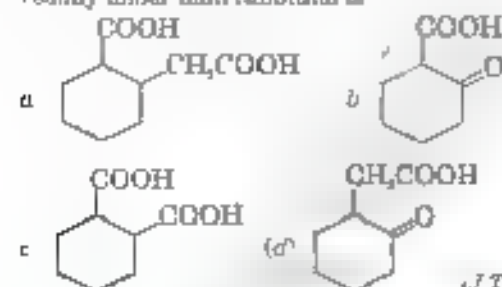


- (a) a hemiacetal (b) an acetal
(c) an ether (d) an ester IIT 2012

- B88.** Among the following compounds, the most acidic is

- (a) *p*-nitrophenol (b) *p*-hydroxybenzoic acid
(c) *o*-hydroxybenzoic acid (d) *p*-toluic acid IIT 2011

- B89.** The compound that undergoes decarboxylation most readily under mild condition is



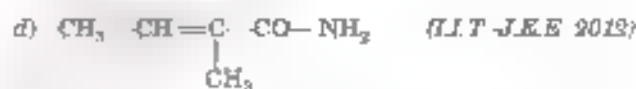
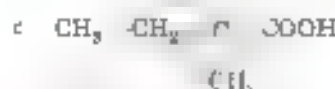
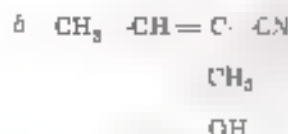
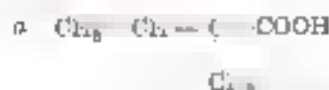
IIT JEE 2012

- B90.** The number of aldol reactions that occurs in the given transformation is

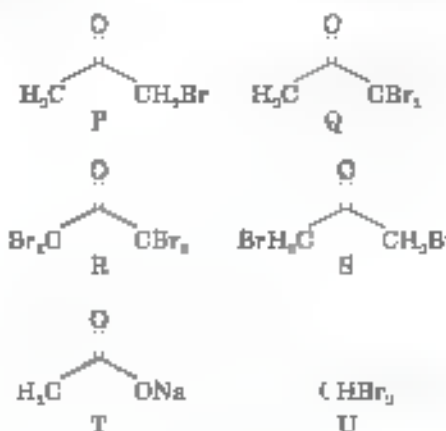
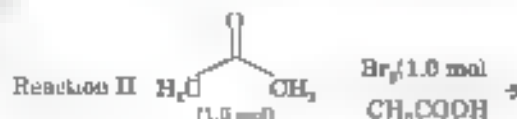
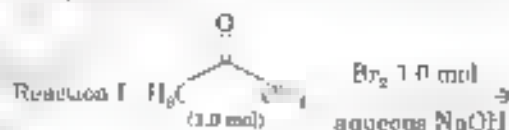


- (a) 1 (b) 2
(c) 3 (d) 4 IIT JEE 2012

- B91.** The major product H of the given reaction sequence is



- B92.** After completion of the reactions I and II, the organic compound(s) in the reaction mixture is (are)



- (a) Reaction I: P and Reaction II: P
(b) Reaction I: U acetone and Reaction II: Q, acetone
(c) Reaction I: T, U, acetone and Reaction II: P
(d) Reaction I: R acetone and Reaction II: S acetone

JEE Advance 2013

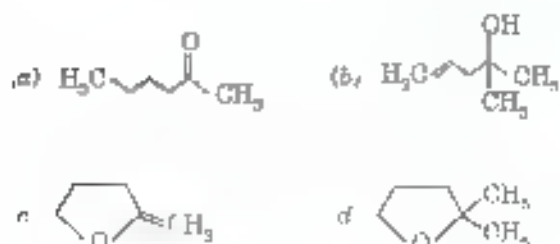
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Competition File

- B83.** The compound that does not liberate CO_2 on treatment with aqueous sodium bicarbonate solution, is
 a. benzoic acid b. benzenesulphonic acid
 c. salicylic acid d. carbonic acid (phenol)

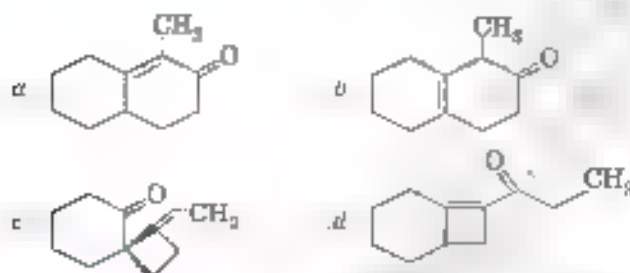
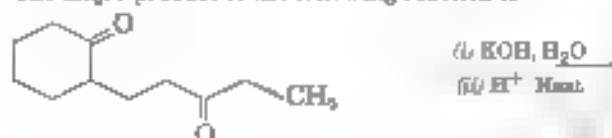
(JEE Advanced 2013)

- B84.** The major product in the following reaction is



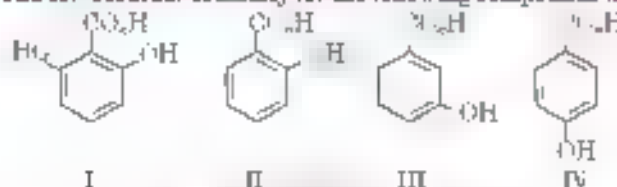
(JEE Advanced 2014)

- B85.** The major product of the following reaction is



(JEE Advanced 2015)

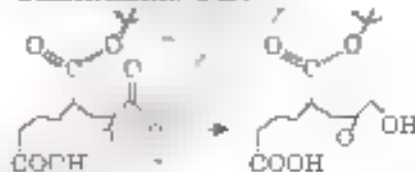
- B86.** The correct order of acidity for the following compounds is



- a. $\text{I} > \text{II} > \text{III} > \text{IV}$ b. $\text{III} > \text{I} > \text{II} > \text{IV}$
 c. $\text{III} > \text{IV} > \text{II} > \text{I}$ d. $\text{I} > \text{II} > \text{IV} > \text{III}$

(JEE Advanced 2016)

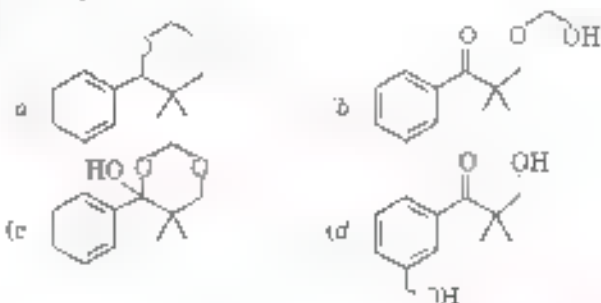
- B87.** Reagent(s) which can be used to bring about the following transformation is/are



- a) LiAlH_4 in $(\text{C}_2\text{H}_5)_2\text{O}$ b) BH_3 in THF
 c) NaBH_4 in $\text{C}_2\text{H}_5\text{OH}$ d) Raney Ni/H_2 in THF

(JEE Advanced 2016)

- B88.** The major product of the following reaction sequence is



(JEE Advanced 2016)

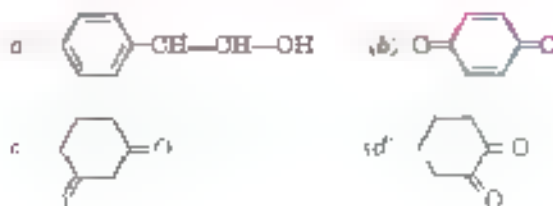
B83. (d) B84. (d) B85. (a) B86. (a) B87. (c) B88. (a)

C (MULTIPLE CHOICE QUESTIONS with more than one correct answer)

- C1.** The Cannizzaro reaction is given by
 (a) benzaldehyde (b) acetaldehyde
 (c) acetone (d) trimethyl acetaldehyde
- C2.** Aldol condensation is not given by
 (a) benzophenone (b) acetophenone
 (c) benzaldehyde (d) propenal

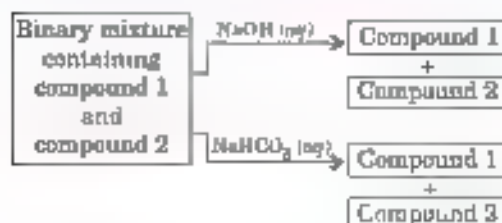
C1. (a, d) C2. (a, c) C3. (a, c)

- C3.** Tautomerisation is exhibited by

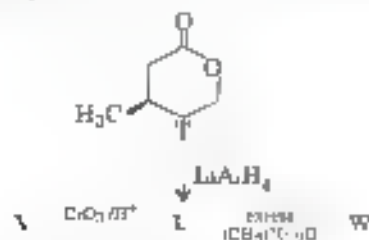


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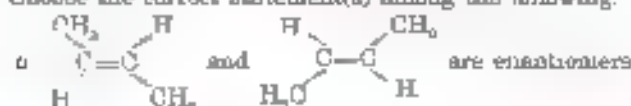
- C4.** Identify the binary mixture(s) that can be separated into individual compounds, by differential extraction, as shown in the given scheme



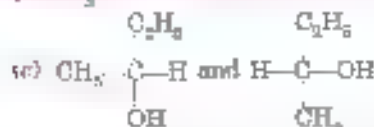
- (a) $\text{C}_6\text{H}_5\text{OH}$ and $\text{C}_6\text{H}_5\text{COOH}$
 (b) $\text{C}_6\text{H}_5\text{COOH}$ and $\text{C}_6\text{H}_5\text{CH}_2\text{OH}$
 (c) $\text{C}_6\text{H}_5\text{CH}_2\text{OH}$ and $\text{C}_6\text{H}_5\text{OH}$
 (d) $\text{C}_6\text{H}_5\text{CH}_2\text{OH}$ and $\text{C}_6\text{H}_5\text{CH}_2\text{COOH}$ (IIT JEE 2013)
- C5.** With reference to the scheme given, which of the given statement(s) about T, U, V and W is/are correct?



- (a) T is soluble in hot aqueous NaOH
 (b) U is optically active
 (c) Molecular formula of W is $\text{C}_{12}\text{H}_{18}\text{O}_4$
 (d) V gives effervescence on treatment with aqueous NaHCO_3 (IIT JEE 2012)
- C6.** Acetophenone is prepared by
- heating benzoyl chloride with dimethyl cadmium
 - treating benzoyl chloride with excess of CH_3MgI followed by hydrolysis
 - treating benzene with excess acetyl chloride in presence of anhydrous AlCl_3
 - reducing benzoyl chloride with H_2 in the presence of Lindlar catalyst
- C7.** Which of the following statements are correct?
- p*-fluoro benzoic acid is weaker acid than *p*-chloro benzoic acid
 - Chloroacetic acid is weaker acid than dichloro acetic acid
 - By passing CO through aqueous NaOH solution at 475 K under 10 atm pressure, formic acid is formed
 - Calcium acetate on heating gives acetic acid
- C8.** Choose the correct statement(s) among the following.

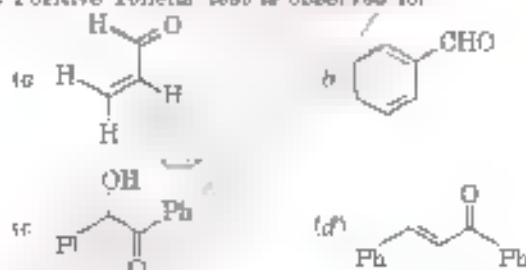


- (b) CH_3CHO on reaction with HCN gives racemic mixture



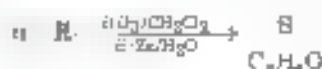
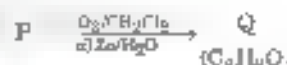
- (d) $\text{CH}_3\text{CH}=\text{NOH}$ shows geometrical isomerism. (WB JEE 2016)

- C9.** Positive Tollens' test is observed for

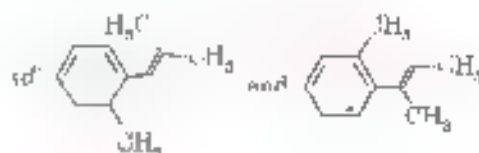
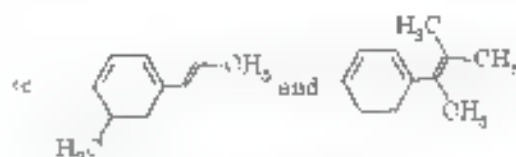
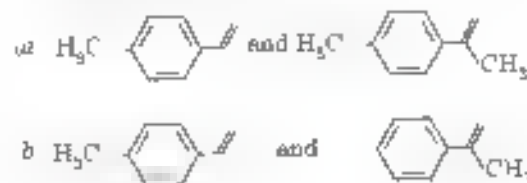


(JEE Advance 2016)

- C10.** Compounds P and R upon ozonolysis produce Q and S respectively. The molecular formula of Q and S is $\text{C}_8\text{H}_8\text{O}$. Q undergoes Cannizzaro reaction but not haloform reaction, whereas S undergoes haloform reaction but not Cannizzaro reaction.

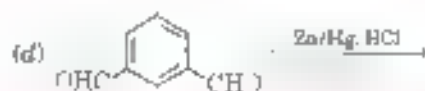
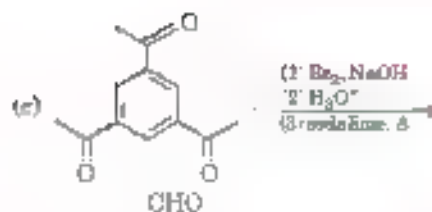


The options with suitable combination of P and R, respectively is/are



(JEE Advance 2017)

C11. The reactions, leading to the formation of 1,3,5-trimethylbenzene are



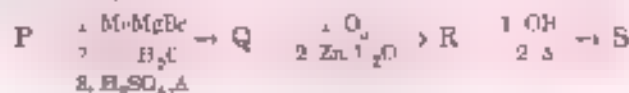
(JEE Advance 2018)

C11 a, b, d

D (MULTIPLE CHOICE QUESTIONS based on the given passage/comprehension

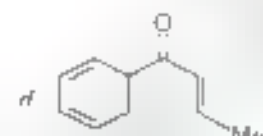
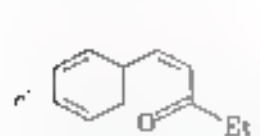
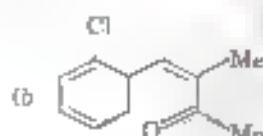
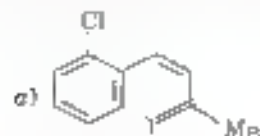
Passage I

A carbonyl compound, P, which gives positive iodoform test, undergoes reaction with MeMgBr followed by dehydration to give an olefin Q. Ozonolysis of Q leads to dicarbonyl compound R, which undergoes intramolecular aldol reaction to give predominantly b

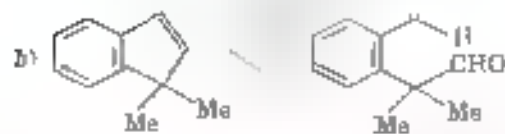
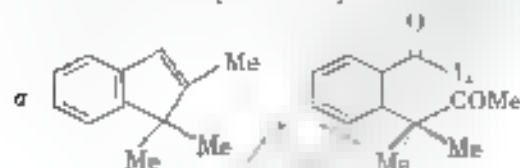


Answer the following questions

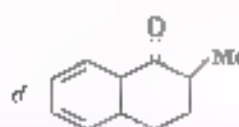
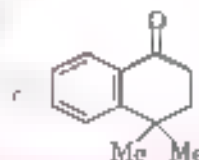
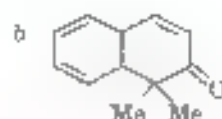
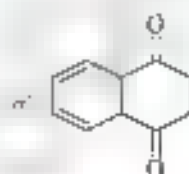
D1. The structure of carbonyl compound P is



D2. The structures of Q and R respectively are



D3. Structure of product S is



Passage II

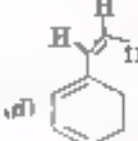
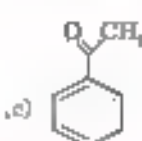
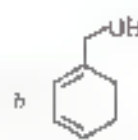
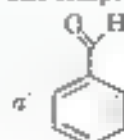
In the following reaction sequence, the compound J is an intermediate



J $\xrightarrow{\text{NaHCO}_3}$ gives effervescence on treatment with NaHCO_3 and a positive Baeyer's test.

Answer the following questions

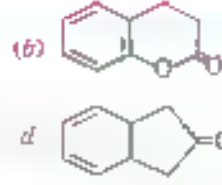
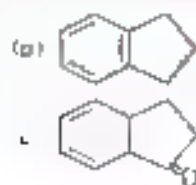
D4. The compound I is



(IIT JEE 2019)

Competition File

D6. The compound **K** is



(c)

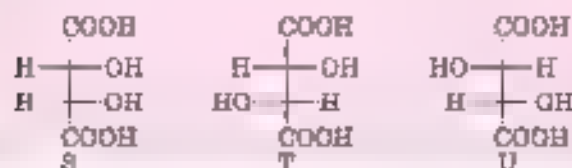
(d)

I.I.T J.E.E. 2013

Passage III

P and Q are isomers of dicarboxylic acid $C_6H_8O_4$. Both decolorize Br_2/H_2O . On heating, P forms the cyclic anhydride.

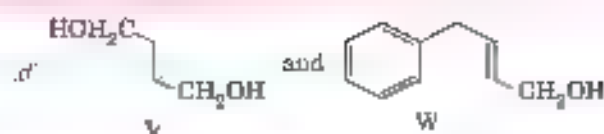
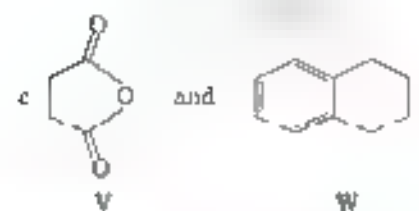
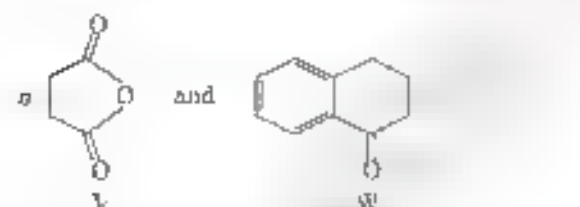
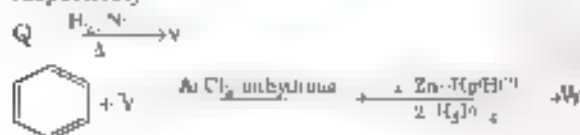
Upon treatment with dilute alkaline $KMnO_4$, P as well as Q could produce one or more than one from S, T and U



Answer the following questions

- D6. Compounds formed from P and Q are respectively
- optically active S and optically active pair T U
 - optically inactive S and optically inactive pair T U
 - optically active pair T U and optically active S
 - optically inactive pair T U and optically inactive S

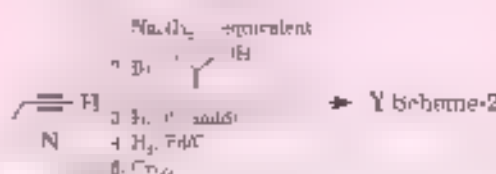
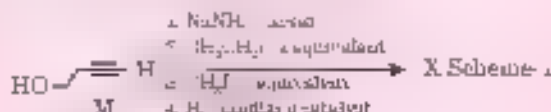
D7. In the following reaction sequences v and W are respectively



JEE Advance 2013

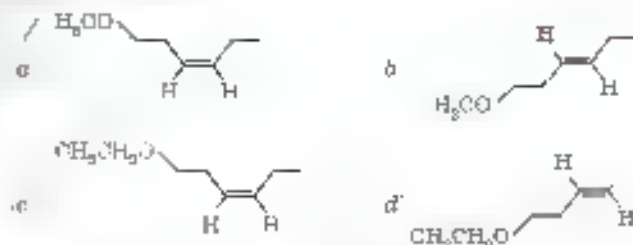
Passage IV

Schemes 1 and 2 describe sequential transformation of alkynes M and N. Consider only the major products formed in each step for both the schemes



Answer the following questions

D8. The product X is



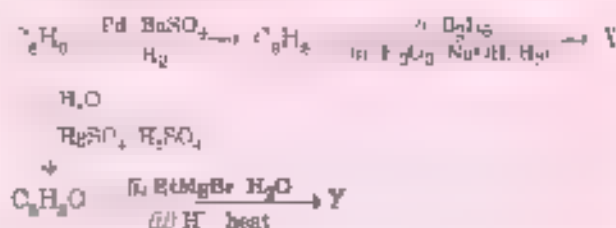
D9. The correct statement with respect to product Y is

- it gives a positive Tollens test and is a functional isomer of X
- it gives a positive Tollens test and is a geometrical isomer of X
- it gives a positive iodoform test and is a functional isomer of X
- it gives a positive iodoform test and is a geometrical isomer of X

JEE Advance 2014

Passage V

In the following reactions:

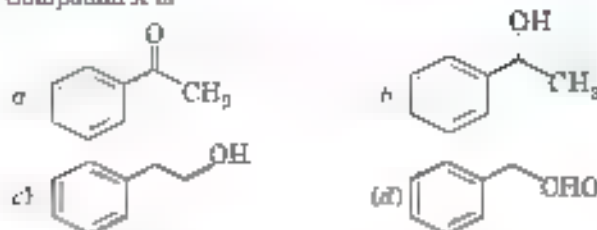


Competition File

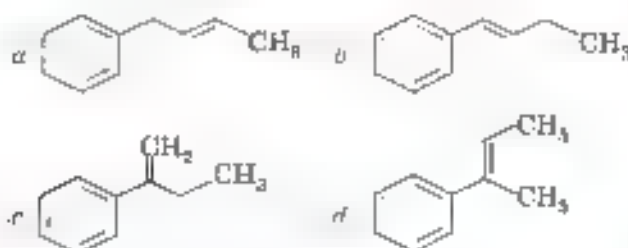
Answer the following questions

(JEE Advance 2017)

D10. Compound X is



D11. The major compound Y is



(JEE Advance 2015)

Passage VI.

Columns 1, 2 and 3 contain starting materials, reaction conditions, and type of reactions, respectively

Column 1	Column 2	Column 3
i. Toluene	NaOH/Br ₂	P. Condensation
ii. Acetophenone	iv. Br ₂ /hv	Q. Carboxylation
iii. Benzaldehyde	iii. CH ₃ CO ₂ O ₂ , CH ₃ COOK	R. Substitution
iv. Phenol	iv. Na, H/CO ₂	S. Aldolism

Answer the following questions:

D12. The only correct combination in which the reaction proceeds through radical mechanism is

- a (ii) iii, R) b) (iii) (ii, iP)
c) (iv) (i, Q) d) (i) (iv, R)

D13. For the synthesis of benzoic acid, the only correct combination is

- a (iii) (iv, R) b) (iv) (ii, P)
c) (ii) (i, S) d) (i) (iv, Q)

D14. The only correct combination that gives two different carboxylic acids is

- a (iv) iii, Q) b) (i) (i, S)
c) (iii) iii, P) d) (ii) (iv, R)

Passage VII.

The reaction of compound P with CH₃MgBr, excess, in (C₂H₅)₂O followed by addition of H₂O gives Q. The compound Q on treatment with H₂SO₄ at 200°C gives R. The reaction of R with "H₂CO" in the presence of anhydrous AlCl₃ in CH₂Cl₂ followed by treatment with H₂ produces compound S. If in compound P is ethyl group

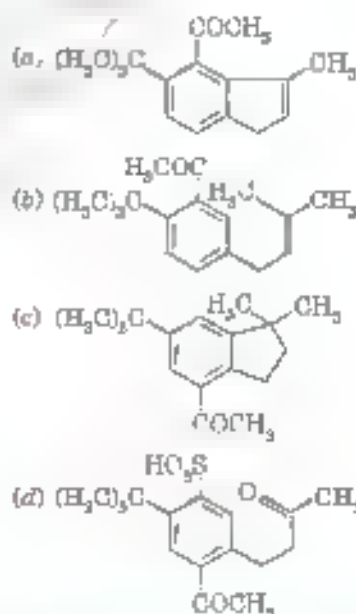


Answer the following questions:

D15. The reactions, Q to R and R to S, are

- (a) Friedel-Crafts alkylation and Friedel-Crafts acylation
(b) dehydration and Friedel-Crafts acylation
(c) Friedel-Crafts alkylation, dehydration and Friedel-Crafts acylation
(d) aromatic sulphonation and Friedel-Crafts acylation

D16. The product S is



(JEE Advance 2017)

Passage VIII

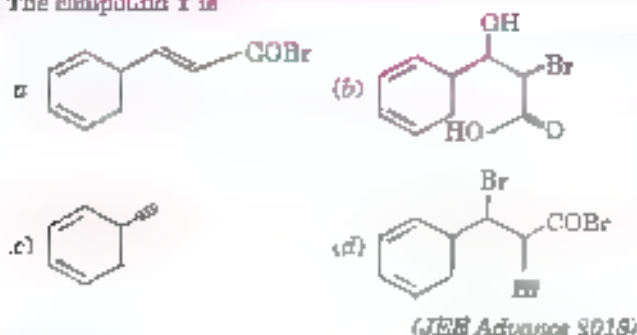
Treatment of benzene with CO/HCl in the presence of anhydrous AlCl₃/CuCl followed by reaction with Ac₂O/NaOAc gives compound X as the major product. Compound X upon reaction with Br₂/Na₂CO₃ followed by heating at 473 K with moist KOH furnishes Y as the major product. Reaction of X with H₂/Pd/C followed by H₃PO₄ isocatalyst gives Z as the major product.

Answers

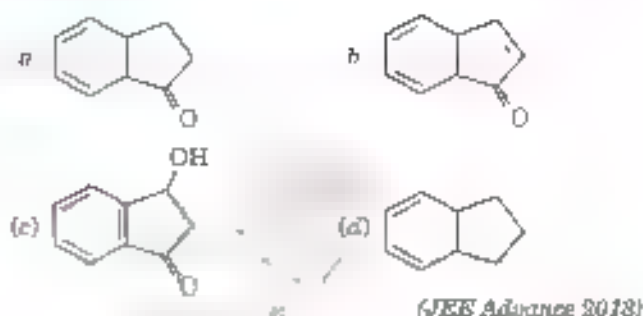
Passage V D10. c) D11. d) Passage VI D12. (d) D13. c) D14. (c) Passage VII D15. b) D16. (c)

Competition File

D17. The compound Y is



D18. The compound Z is



Passage VIII. D17. c) D18. b)

Assertion Reason Type Questions

The questions given below consist of an Assertion and Reason. Use the following key to choose the appropriate answer.

- a) If both assertion and reason are CORRECT and reason is the 'CORRECT' explanation of the assertion.
 b) If both assertion and reason are CORRECT but, reason is NOT THE CORRECT explanation of the assertion.
 c) If assertion is CORRECT but, reason is INCORRECT.
 d) If assertion is INCORRECT but, reason is CORRECT.
 e) If both assertion and reason are INCORRECT.

- Assertion :** Pentan-2-one can be distinguished from pentan-3-one by iodoforn test.
Reason : Former is methyl ketone while the latter is not.
- Assertion :** In methanal, all the four atoms are in the same plane.
Reason : The carbon atom in methanal is sp^2 hybridized.
- Assertion :** Benzaldehyde is more reactive than propanal towards nucleophilic addition reactions.
Reason : Benzaldehyde is less sterically hindered.
- Assertion :** Acetaldehyde undergoes aldol condensation with dil. NaOH .
Reason : Aldehydes which do not contain α -hydrogen undergo aldol condensation.

- Assertion :** Reduction of 3-phenylprop-2-enal with LiAlH_4 gives 3-phenylpropan-1-ol.

Reason : Both aldehyde group and double bond of α, β -unsaturated aldehydes are reduced by LiAlH_4 .

- Assertion :** Cross Cannizzaro's reaction between methanal and benzaldehyde gives benzyl alcohol and formate ion.

Reason : Benzaldehyde does not contain α -hydrogen atom.

- Assertion :** The pK_a of acetic acid is lower than that of phenol.

Reason : Phenoxide ion is more resonance stabilized than acetate ion. (A.I.M.S. 2004)

- Assertion :** Benzoic acid and phenol can be distinguished by NaHCO_3 .

Reason : Benzoic acid is stronger acid than phenol.

- Assertion :** Fluoroacetic acid is stronger acid than chloroacetic acid.

Reason : Due to greater electron donating effect of F than Cl.

- Assertion :** Ethanoic acid liberates hydrogen with sodium metal.

Reason : Sodium is an alkali metal.

- Assertion :** Acetic acid does not undergo haloform reaction.

Reason : Acetic acid has no α -hydrogen atom.

- Assertion :** Acetic acid is weaker acid than $\text{CH}_3\text{CH}_2\text{COOH}$.

Reason : due to +I effect of methyl group.

1. a) 2. c) 3. a) 4. c) 5. e) 6. b) 7. c) 8. b) 9. c) 10. b) 11. c) 12. a)

Competition File

Matrix Match Type Questions

Each question contains statements given in two columns, which have to be matched. Statements in Column I are labelled as A, B, C and D whereas statements in Column II are labelled as p, q, r and s. Match the entries of Column I with appropriate entries of Column II. Each entry in Column I may have one or more than one correct option from Column II. The answers to these questions have to be appropriately bubbled as illustrated in the following example:



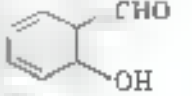
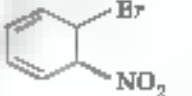
	p	q	r	s
A	<input type="radio"/>	<input type="radio"/>	<input checked="" type="radio"/>	<input type="radio"/>
B	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input checked="" type="radio"/>
C	<input type="radio"/>	<input type="radio"/>	<input checked="" type="radio"/>	<input type="radio"/>
D	<input type="radio"/>	<input checked="" type="radio"/>	<input type="radio"/>	<input type="radio"/>

If the correct matches are A-q, A-r, B-p, B-s, C-r, C-s and D-q, then the correctly bubbled matrix will look like the following:

1. Match the compounds/ions in Column I with their properties/reactions in Column II.

Column I	Column II
(A) C_6H_5CHO	(p) gives precipitate with 2, 4-DNP
(B) $CH_3C\equiv CH$	(q) gives precipitate with $AgNO_3$
(C) CN^-	(r) is a nucleophile
(D) I^-	(s) is involved in cyanohydrin formation.

2. Match each of the compounds given in Column I with the reaction(s), that they can undergo, given in Column II.

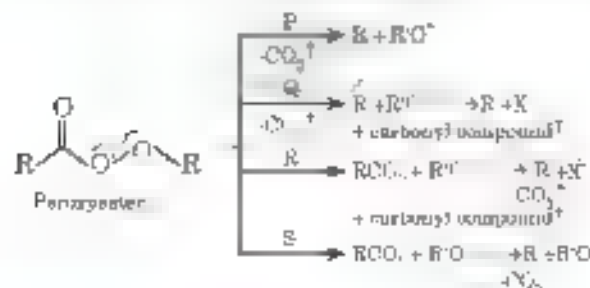
Column I	Column II
(A) 	(p) Nucleophilic substitution
(B) 	(q) Elimination
(C) 	(r) Nucleophilic addition
(D) 	(s) Esterification with acetic acid
	(t) dehydrogenation.

1. A	p, s	B)	r	C	q, r, s	D)	q, r
(2) A	p, q, r	B)	p, s, t	C	r, s	E	p

Matching List Type Questions

The following question has two matching lists. Choices for the correct combination of elements from List-I and List-II are given as options a, b, c and d out of which one is correct.

1. Different possible thermal decomposition pathways for peroxyesters are shown below. Match each pathway from List I with an appropriate structure from List-II and select the correct answer using the code given below the lists.



List-I

(P) Pathway P

(Q) Pathway Q

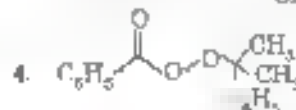
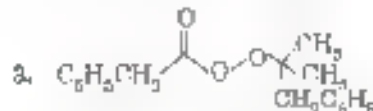
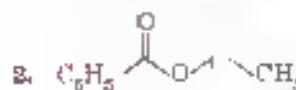
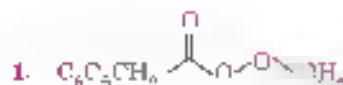
(R) Pathway R

(S) Pathway S

Code

	P	Q	R	S
a	1	2	4	2
b	2	4	3	1
c	4	1	2	3
d	3	3	1	4

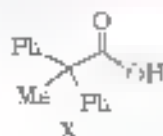
List-II



(JEE Advanced 2019)

Competition File

3. The desired product **X** can be prepared by reacting the major product of the reactions in List-I with one or more appropriate reagents in List-II, given, order of migratory aptitude: aryl > alkyl > hydrogen



List-I	List-II
<p>P + H_2SO_4</p>	1. I_2, NaOH
<p>Q + HNO_3</p>	2. $(\text{Ag}(\text{NH}_3)_2)\text{OH}$

List-I	List-II
<p>R + H_2SO_4</p>	3. Fehling solution
<p>S + AgNO_3</p>	4. HCHO, NaOH

The correct option is

- A) **P** \rightarrow 2, **Q** \rightarrow 2, 3, **R** \rightarrow 1, 4, **S** \rightarrow 2, 4
 B) **P** \rightarrow 1, 5; **Q** \rightarrow 3, 4, **R** \rightarrow 4, 5; **S** \rightarrow 3
 C) **P** \rightarrow 1, 5; **Q** \rightarrow 3, 4, **R** \rightarrow 5; **S** \rightarrow 2, 4
 D) **P** \rightarrow 1, 5; **Q** \rightarrow 2, 3, **R** \rightarrow 1, 5; **S** \rightarrow 2, 3

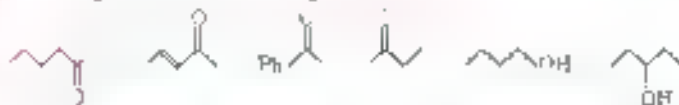
JEE Advanced 2018

Integer Type Questions

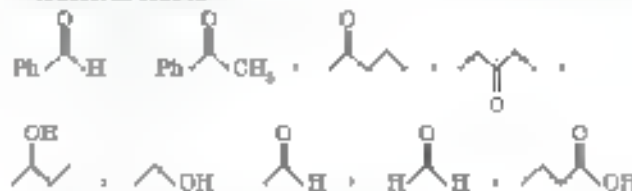
Integer Type: The answers to each of the following question is a single digit integer ranging from 0 to 9.

- The total number of isomeric aldehydes and ketones having the molecular formula $\text{C}_6\text{H}_{10}\text{O}$ are
- The number of compounds which undergo aldol condensation in the following list of compounds are: methanal, 2-methylpentanal, cyclohexan-1-one, benzaldehyde, 1-phenylpropanone, phenylacetaldehyde, 2,2-dimethylbutanal, benzophenone, propenone.
- The number of isomeric ketones having the molecular formula $\text{C}_6\text{H}_{12}\text{O}$ which give iodoform test are
- The number of compounds amongst : methanal, benzaldehyde, propanal, propanone, 2,2-dimethylpropanal, 3-methylpentanal which give Cannizzaro's reaction are
- The number of reagents which convert aldehyde or ketones to alkanes in the following list are: NaBH_4 , NH_2NH_2 , KOH , HI and P ; H_2 , Ni , Zn/Hg , HCl , LiAlH_4 , Pt , acidified KMnO_4 , alkaline KMnO_4 .

6. The number of compounds which don't react with Tollens reagent in the following list is



7. The number of compounds among the following which give iodoform test is



8. The number of compounds which are more acidic than benzoic acid amongst : *o*-nitrobenzoic acid, *p*-chlorobenzoic acid, *p*-methoxybenzoic acid, *p*-toluic acid, *o*-toluic acid, acetic acid, *o*-hydroxybenzoic acid are

9. The number of carboxylic acids which are more acidic than acetic acid amongst the following are:

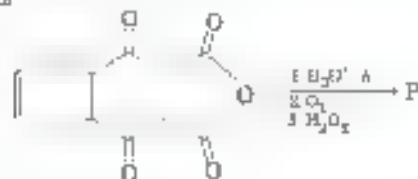


Competition File

10. The number of carbon atoms in adipic acid is
11. The number of compounds having boiling point higher than acetic acid in the following set of compounds is

- (i) $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$
- (ii) HCOOH
- (iii) $\text{C}_2\text{H}_5\text{COOH}$
- (iv) CH_3COCH_3
- (v) $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$
- (vi) $\text{C}_3\text{H}_7\text{COOH}$

12. The total number of carboxylic acid groups in the product P is

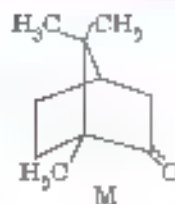


(JEE Advance 2013)

13. Consider all possible isomeric ketones, including stereoisomers of MW = 100. All these isomers are independently reacted with NaBH_4 (Note: Stereoisomers are also reacted separately). The total number of ketones that give a racemic product(s), is/are:

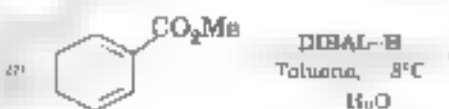
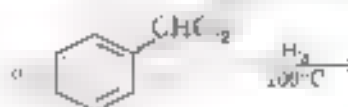
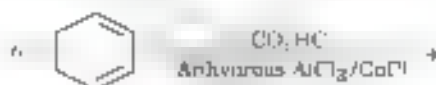
(JEE Advance 2011)

14. The total number of stereoisomers that can exist for M is



(JEE Advance 2015)

15. Among the following, the number of reaction(s) that produce(s) benzaldehyde is



(JEE Advance 2015)

10. C 11. 2 12. 2 13. 5 14. 2 15. 4



NCERT

Exemplar Problems

Objective Questions

Multiple Choice Questions (Type-I)

1. Addition of water to alkynes occurs in acidic medium and in the presence of Hg^{2+} ions as a catalyst. Which of the following products will be formed on addition of water to but-1-yne under these conditions.



Competition File

2. Which of the following compounds is most reactive towards nucleophilic addition reactions?



3. The correct order of increasing acidic strength is

- a) Phenol < Ethanol < Chloroacetic acid < Acetic acid
 b) Ethanol < Phenol < Chloroacetic acid < Acetic acid
 c) Ethanol < Phenol < Acetic acid < Chloroacetic acid
 d) Chloroacetic acid < Acetic acid < Phenol < Ethanol

4. Compound $\text{Ph}-\text{O}-\text{C}(=\text{O})-\text{Ph}$ can be prepared by the reaction of

- a) Phenol and benzoic acid in the presence of NaOH
 b) Phenol and benzoyl chloride in the presence of pyridine
 c) Phenol and benzoyl chloride in the presence of ZnCl_2
 d) Phenol and benzaldehyde in the presence of palladium

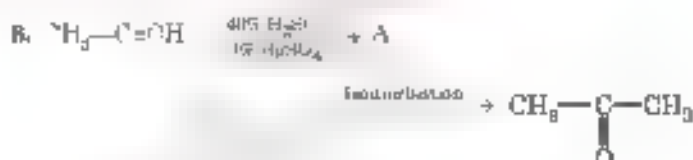
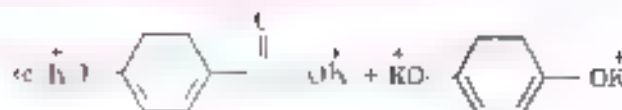
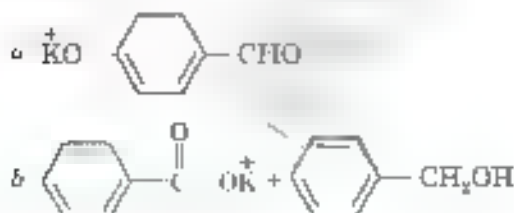
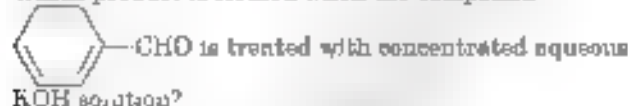
5. The reagent which does not react with both, acetone and benzaldehyde

- a) Sodium hydrogensulphite
 b) Phenyl hydrazine
 c) Fehling's solution
 d) Grignard reagent

6. Cannizzaro's reaction is not given by



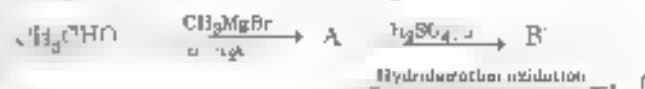
7. Which product is formed when the compound



Structure of A and type of isomerism in the above reaction are respectively

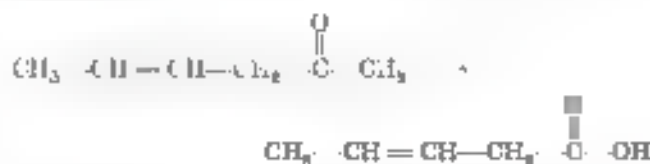
- a) Prop-1-en-2-ol metamerism
 b) Prop-1-en-2-ol tautomerism
 c) Prop-1-en-2-ol geometrical isomerism
 d) Prop-1-en-2-ol tautomerism

9. Compounds A and C in the following reaction are



- a) identical b) positional isomers
 c) functional isomers d) optical isomers

10. Which is the most suitable reagent for the following conversion?



- a) Tollen's reagent b) Benzoyl peroxide
 c) I_2 and NaOH solution d) Sn and NaOH solution

11. Which of the following compounds will give butanone on oxidation with alkaline KMnO_4 solution?

- a) Butan-1-ol b) Butan-2-ol
 c) Both of these d) None of these

12. In Clemmensen Reduction carbonyl compound is treated with

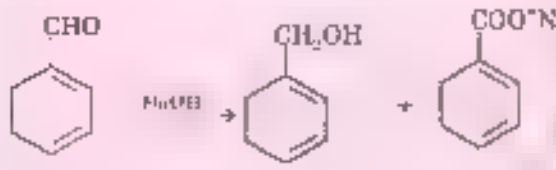
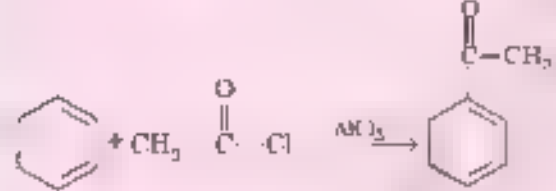
- a) Zinc amalgam + HCl
 b) Sodium amalgam + HCl
 c) Zinc amalgam + nitric acid
 d) Sodium amalgam + HNO_3

Competition File

21. Match the reactions given in Column I with the suitable reagents given in Column II

Column I (Reactions)	Column II (Reagents)
a) Benzophenone \rightarrow Diphenylmethane	(i) LiAlH_4
b) Benzaldehyde \rightarrow 1-Phenylethanol	(ii) DIBAL-H
c) Cyclohexanone \rightarrow Cyclohexanol	(iii) Zn(Hg)/Conc. HCl
d) Phenyl benzoate \rightarrow Benzaldehyde	(iv) CH_3MgBr

22. Match the example given in Column I with the name of the reaction in Column II

Column I Example	Column II (Reaction)
a $\text{CH}_3\text{COCl} + \text{H}_2 \xrightarrow{\text{Pd-Pt/BaSO}_4} \text{CH}_3\text{CHO}$	Friedel Crafts acylation
b 	(i) IIVZ reaction
c 	(ii) Aldol condensation
d $\text{R-CH}_2\text{CH}_2\text{NH}_2 \xrightarrow{\text{Br}_2/\text{Red P}} \text{R-CH(Br)-COOH}$	(iii) Cannizzaro's reaction
e $\text{CH}_3\text{CN} \xrightarrow[\text{H}^+]{\text{SnCl}_4/\text{HCl}} \text{CH}_3\text{CHO}$	(iv) Rosenmund's reduction
f $2\text{CH}_3\text{CHO} \xrightarrow{\text{NaOH}} \text{CH}_3\text{CH}=\text{CHCHO}$	(v) Stephen's reaction

21. a) (i), b) (iv), c) (ii), d) (iii)

22. (a), (v); (b) (ii); (c) (i), (d) (iii), (e) (iv), (f) (v)

Competition File

Note: In the following questions a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices.

- Assertion and reason both are correct and reason is correct explanation of assertion.
- Assertion and reason both are wrong statements.
- Assertion is correct statement but reason is wrong statement.
- Assertion is wrong statement but reason is correct statement.
- Assertion and reason both are correct statements but reason is not correct explanation of assertion.

23. Assertion: Formaldehyde is a planar molecule.

Reason: It contains sp^2 hybridised carbon atom.

24. Assertion: Compounds containing $-CHO$ group are easily oxidised to corresponding carboxylic acids.

Reason: Carboxylic acids can be reduced to alcohols by treatment with $LiAlH_4$.

25. Assertion: The α -hydrogen atom in carbonyl compounds is less acidic.

Reason: The anion formed after the loss of α -hydrogen atom is resonance stabilised.

26. Assertion: Aromatic aldehydes and formaldehyde undergo Cannizzaro reaction.

Reason: Aromatic aldehydes are almost as reactive as formaldehyde.

27. Assertion: Aldehydes and ketones, both react with Tollen's reagent to form silver mirror.

Reason: Both aldehydes and ketones contain a carbonyl group.

23. (a) 24. (e) 25. (d) 26. (c) 27. (d)

Hints & Explanations for Difficult Objective Type Questions

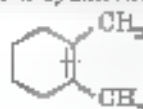
A. mcq with only one correct answer

A6. b Cannizzaro's reaction is given by aldehydes which do not contain α -hydrogen. Therefore, $HCHO$ does not give this reaction.

A7. b The compounds containing $(^+H_3C)_2$ or $^+H_3C-H-C-H$ group give iodoform test.

A8. (a) $RCHO + 4H \xrightarrow[HCl]{Zn/Hg} R-CH_2 + H_2$ Clemmensen reduction
Alkane

A9. d The product of ozonolysis is a single product and is symmetrical with same number of carbon atoms. It is



A10. (a) $CH_3CHO \xrightarrow{BF_3} CH_3-C(OH)(CN)-CH_3 \xrightarrow{H^+/H_2O} CH_3CHOH-COOH$
Lactic acid

A11. b $HC \equiv CH \xrightarrow[H]{Hg^{2+}/H^+} CH_3CH_2 \xrightarrow{LiAlH_4} CH_3CH_2 \xrightarrow{PBr_3} CH_3CH_2Br$

A12. (e) $CH_3COCH_3 \xrightarrow{H^+/H_2O} CH_3C(OH)(CH_3)CH_2COCH_3 \xrightarrow{H^+} CH_3C(OH)(CH_3)CH_2COCH_3$

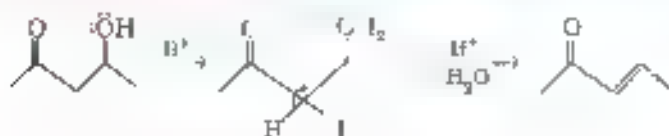
A13. (a) $CH_3COCl \xrightarrow[H_2O]{Pd/H_2} CH_3CHO$
Acetaldehyde

Competition File

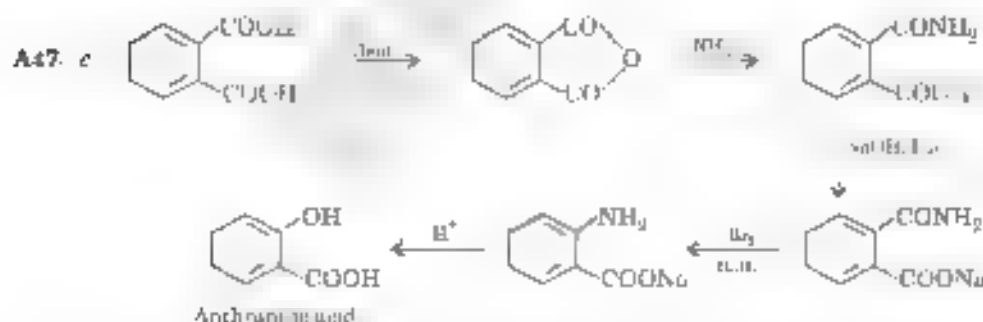
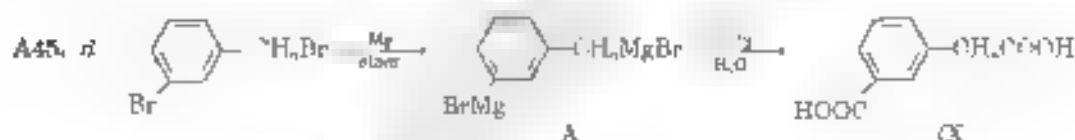
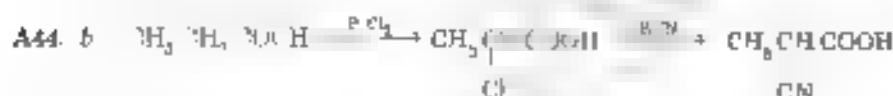
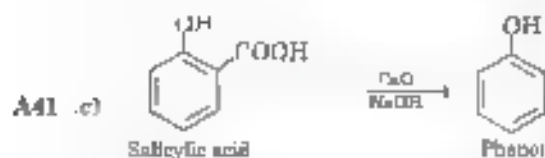
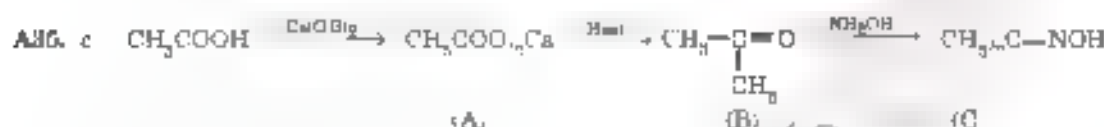
- A14. b** $\text{CH}_3\text{CH}_2\text{C}(=\text{O})\text{CH}_2\text{CH}_3 \xrightarrow[\text{(ii) } \text{H}_3\text{O}^+]{\text{C}_2\text{H}_5\text{MgBr}}$ $\text{CH}_3\text{CH}_2\text{C}(\text{OH})(\text{C}_2\text{H}_5)\text{CH}_2\text{CH}_3 \xrightarrow{\text{H}_3\text{O}^+}$ $\text{CH}_3\text{CH}_2\text{C}(\text{C}_2\text{H}_5)=\text{CHCH}_3$
 Diethyl ketone Diethyl ketone Acetaldehyde
- A16. c** $\text{CH}_3\text{CH}_2\text{CH}_2\text{C}(=\text{O})\text{H} + \text{CH}_3\text{CH}_2\text{C}(=\text{O})\text{H} \xrightarrow{^-\text{OH}}$ $\text{CH}_3\text{CH}_2\text{CH}_2\text{OCH}(\text{CH}_2\text{CH}_3)\text{CHO}$
 Butanal Ethyl propyl acetal
- A17. b** $\text{HCHO} + \text{CH}_3\text{MgBr} \xrightarrow{\text{dry ether}}$ $\text{H}-\text{C}(\text{OH})(\text{CH}_3)\text{OMgBr} \xrightarrow{\text{H}^+/\text{H}_2\text{O}}$ $\text{CH}_3\text{CH}_2\text{OH} + \text{MgBrOH}$
Primary alcohol
- A18. d** $m\text{-chlorobenzaldehyde} + m\text{-chlorobenzaldehyde} \xrightarrow[\text{Cannizzaro's reaction}]{\text{conc. KOH}}$ $m\text{-chlorobenzyl alcohol} + m\text{-chlorobenzoate}$
m-Chlorobenzyl alcohol Potassium m-chlorobenzoate
- A19. b** $\text{CH}_3\text{CH}_2\text{CHO} + \text{CH}_3\text{CH}_2\text{CHO} \xrightarrow{^-\text{OH}}$ $\text{CH}_3\text{CH}_2\text{CH}(\text{OH})\text{CH}_2\text{CHO}$ or $\text{CH}_3\text{CH}_2\text{CH}(\text{OH})\text{CH}(\text{CH}_3)\text{CHO}$
 Propanaldehyde Hydroxybutanal
- A21. (b)** $\text{C}_6\text{H}_5\text{CHO} + \text{C}_6\text{H}_5\text{CHO} \xrightarrow[\text{Cannizzaro's reaction}]{\text{conc. NaOH}}$ $\text{C}_6\text{H}_5\text{CH}_2\text{OH} + \text{C}_6\text{H}_5\text{COO}^-\text{Na}^+$
Benzyl alcohol
- A22. (b)** $\text{CH}_3\text{CHO} + \text{CH}_2\text{CHO} \xrightarrow{\text{OH}^-}$ $\text{CH}_3\text{CH}(\text{OH})\text{CH}_2\text{CHO}$
- A25. b** $\text{CH}_3\text{CO} + \text{HCN} \rightarrow \text{CH}_3\text{C}(\text{OH})(\text{CN})\text{CH}_3 \xrightarrow{\text{H}^+/\text{H}_2\text{O}}$ $\text{CH}_3\text{C}(\text{OH})(\text{COOH})\text{CH}_3 \xrightarrow[\text{Heat}]{\text{H}_2\text{SO}_4}$ $\text{CH}_2=\text{C}(\text{COOH})\text{CH}_3$
- A26. b** $\text{CH}_3\text{CH}_2\text{CHO} \xrightarrow{\text{HCN, H}^+/\text{H}_2\text{O}}$ $\text{CH}_3\text{CH}_2\text{CH}(\text{OH})\text{CN} \xrightarrow{\text{LiAlH}_4}$ $\text{CH}_3\text{CH}_2\text{CH}(\text{OH})\text{CH}_2\text{NH}_2$
- A28. (a)** $\text{CH}_3\text{CHO} \xrightarrow{\text{HCN}}$ $\text{CH}_3\text{C}(\text{OH})(\text{CN})\text{CH}_3 \xrightarrow{\text{H}^+/\text{H}_2\text{O}}$ $\text{CH}_3\text{CH}(\text{OH})\text{COOH}$
 Acetaldehyde Cyanohydrin Lactic acid
- A29. c** $\text{CH}_3\text{CH}(\text{Cl})\text{CHO} \xrightarrow[\text{red. NaBH}_4]{\text{H}_2}$ $\text{CH}_3\text{CH}_2\text{CHO}$
Propanal
- $\text{CH}_3\text{CH}(\text{Cl})\text{CHO} \xrightarrow[\text{dry ethe.}]{\text{H}_2\text{O}_2/\text{H}^+}$ $\text{CH}_3\text{CH}_2\text{COCH}_3$
Butan-2-one

Competition File

A30. a β -hydroxy aldehydes or β -hydroxy ketones readily undergo dehydration to give α , β -unsaturated aldehydes or ketones



A33. (a) *m*-Nitro benzoic acid is meta directing



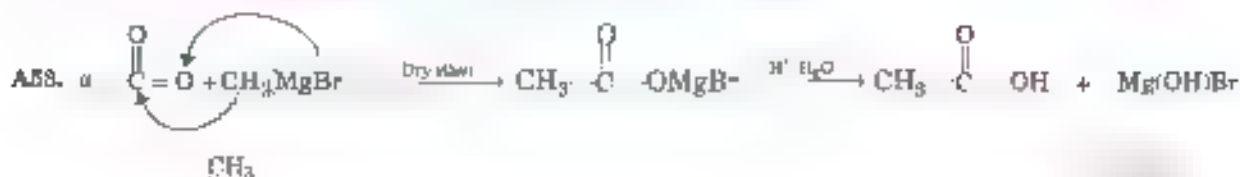
A48. c The carboxylic acids have higher boiling points because they form associated molecules due to H-bonding.

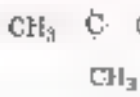
A50. (c) Picric acid is trinitrophenol and does not have carboxyl group



Competition File

A52. (d) Formic acid gives silver mirror test while acetic acid does not

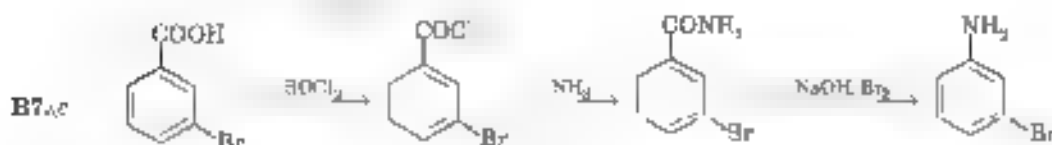
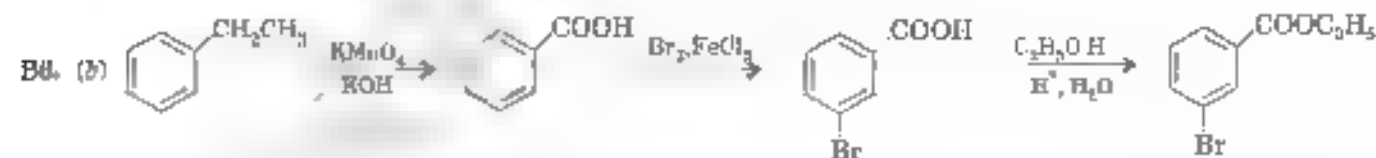
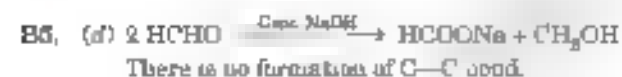
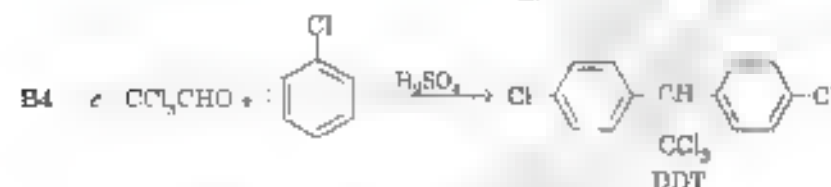
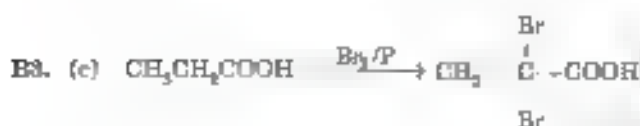
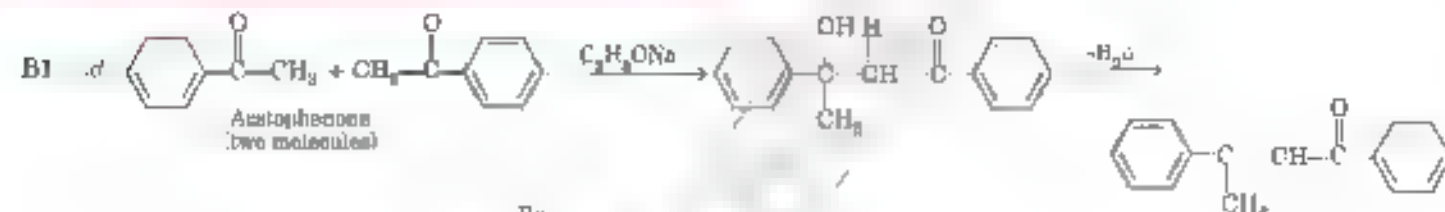


A54. b  does not contain α -hydrogen and therefore, will not undergo Hell-Volhard-Zelinsky reaction
2,2-Dimethylpropanoic acid

A55. b) Position (x) is most acidic because of $-\text{COOH}$ group.

NH_2 group at position y is more acidic than x because of the presence of electron withdrawing $-\text{COOH}$ group in close proximity

B. mcq from Competitive Examinations

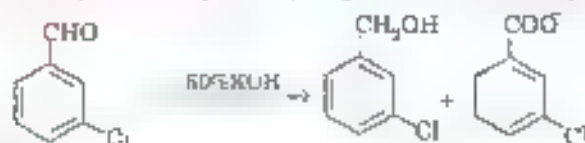


B8. b Carbonyl group can be reduced to $-\text{CH}_2$ group with zinc amalgam and conc. HCl . This reaction is known as Clemmensen's reaction.

B9. b CH_3CHO and $\text{C}_6\text{H}_5\text{CH}_2\text{CHO}$ can be distinguished by iodoform test because CH_3CHO will give iodoform test but $\text{C}_6\text{H}_5\text{CH}_2\text{CHO}$ will not.

Competition File

B10. c Aldehydes having no α -hydrogen atoms on heating with conc. KOH 50% undergo Cannizzaro's reaction.



B11. a As I effect increases, COOH group becomes more electron deficient and tendency to lose H^+ increases and therefore, acidic strength increases. Hence $\text{CF}_3\text{COOH} > \text{Cl}_3\text{CH}_2\text{COOH} > \text{CH}_3\text{COOH}$. As I effect increases, acidic strength decreases. i.e. $\text{CH}_3\text{COOH} > \text{H}_2\text{CH}_2\text{COOH} > \text{H}_3\text{CH}_2\text{COOH}$. Thus correct order: $\text{CF}_3\text{COOH} > \text{Cl}_3\text{CH}_2\text{COOH} > \text{H}_3\text{CH}_2\text{COOH} > \text{H}_2\text{CH}_2\text{COOH}$.



b) Reduction in the presence of Zn/Hg and conc. HCl is used for aldehydes and ketones but carboxylic acid group remains unaffected.



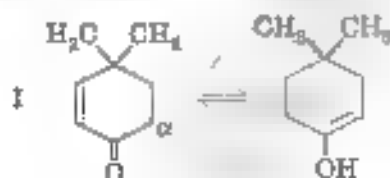
B13. d Electron withdrawing group NO_2 facilitates the nucleophilic attack.

B14. c *o*-Nitrophenol is a weaker acid than HCO_3^- and hence it does not react with NaHCO_3 . Therefore *o*-nitrophenol will not be soluble in sodium hydrogen carbonate solution.

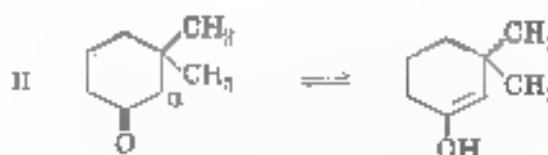
B16. a Since the compound gives phenyl hydrazine test, it must be an aldehyde or a ketone. For iodoform test, there must be $\text{CH}_3-\text{C}(=\text{O})$ group and for Tollen's test $-\text{CHO}$ group is required. Hence $\text{CH}_3-\text{C}(=\text{O})$ and $-\text{CHO}$ groups are absent. It gives *n*-pentane on reduction and, therefore, it is a straight chain compound. The compound is



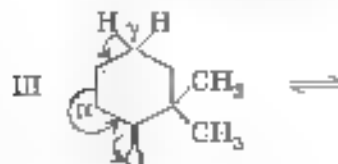
B17. b) All the three



In the case, α -H participates.

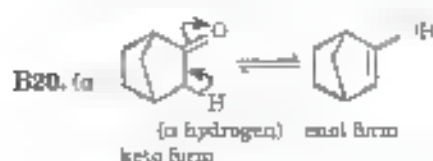
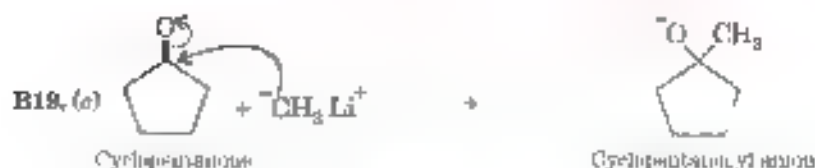
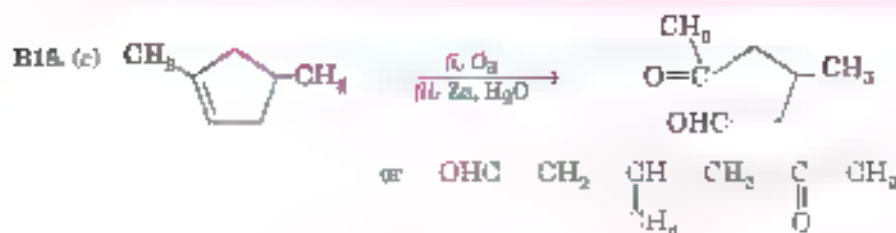


In the case, α -H participates

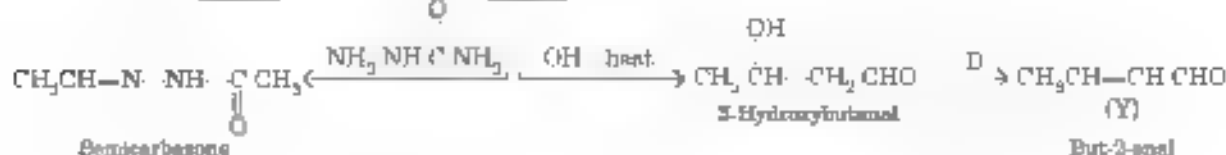
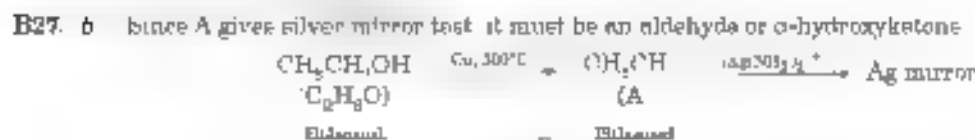
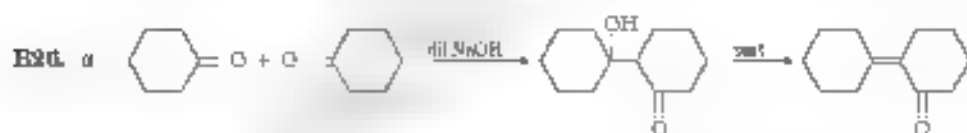
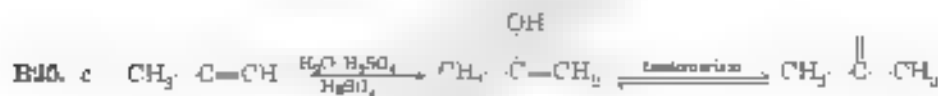
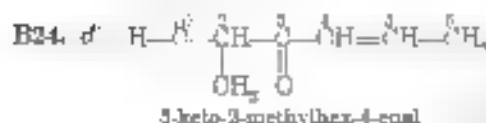
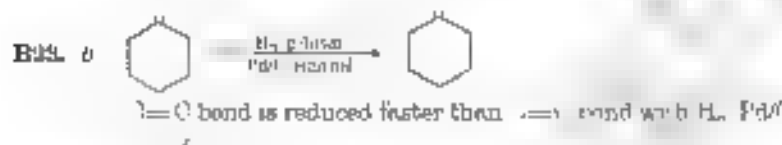
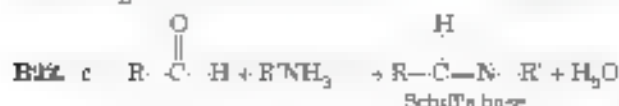


In this case γ -H participates

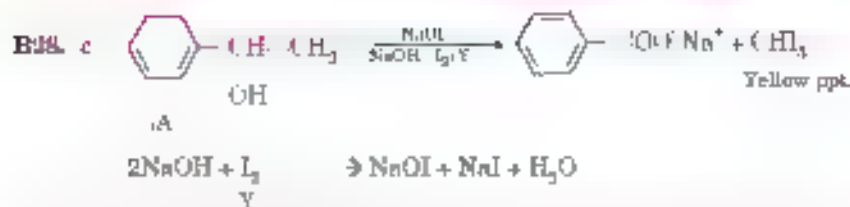
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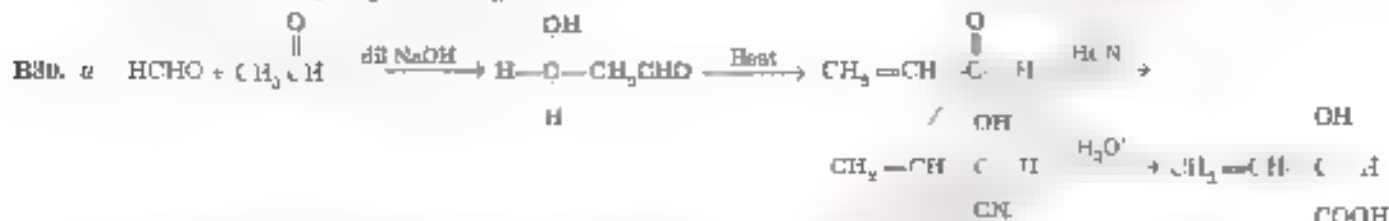
α -hydrogens at bridged carbon atoms do not participate in tautomerism. Therefore, I and II which contain α -hydrogens at bridged carbon atoms do not show tautomerism. Only structure III shows tautomerism.



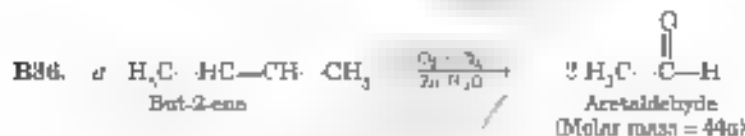
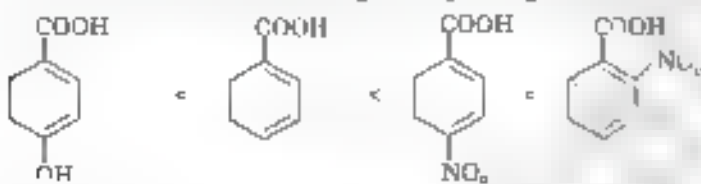
Competition File



B39. d) Carboxylic acids have higher boiling points than aldehydes, ketones or even alcohols because of association through intermolecular hydrogen bonding.



B41. d) Electron donating groups tend to decrease acidic character while electron withdrawing groups tend to increase acidic character. The effect of substituents on acidity is more pronounced at *p*-position than at *o*-position. Moreover *o*-substituted benzoic acids are generally stronger acids than benzoic acid known as *ortho* effect. Thus, correct order is



B47. b) Stronger the acid, weaker is the conjugate base.

Base + Proton \rightarrow Conjugate acid

Conjugate acid formed will be RCOOH , NH_2 , $\text{HC}=\text{CH}$, CH_4

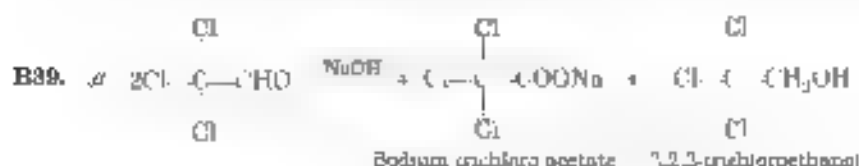
Acidic strength follows order

$\text{RCOOH} > \text{HC}=\text{CH} > \text{NH}_2 > \text{CH}_4$

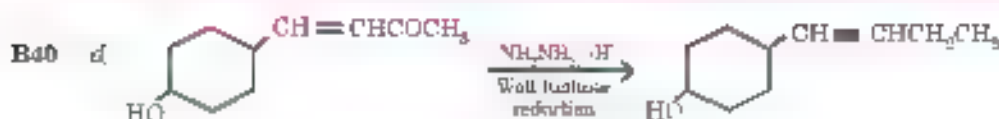
Increasing basicity will be

$\text{RCOO}^- < \text{HC}=\text{C}^- < \text{NH}_2^- < \text{CH}_3^-$

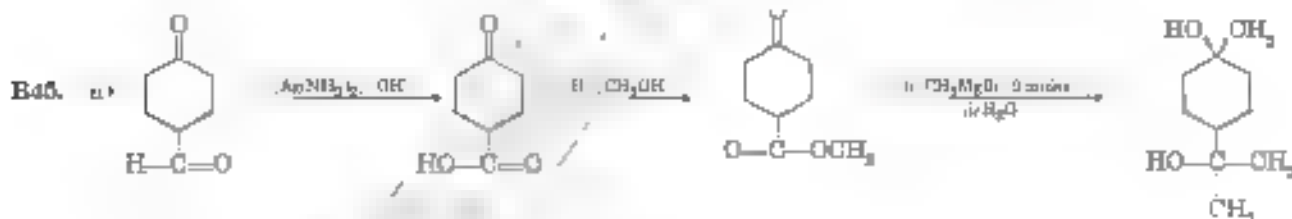
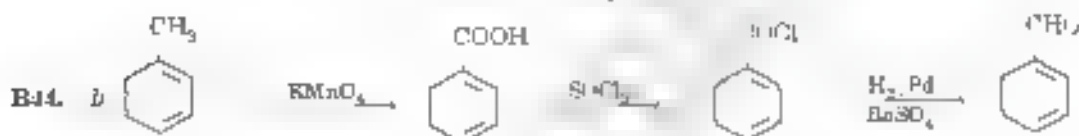
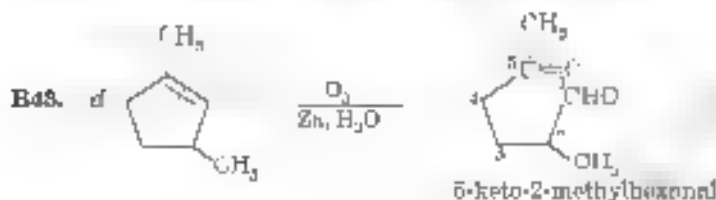
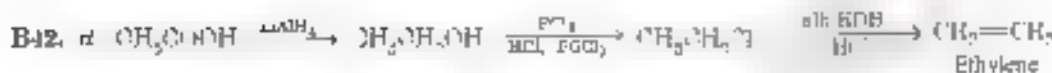
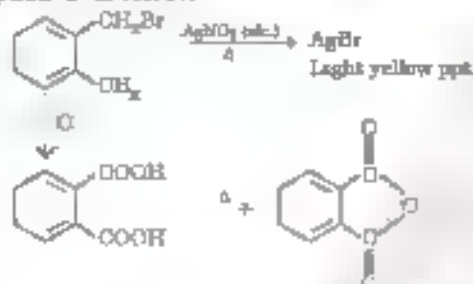
B48. d) Phenol gives violet colour with neutral FeCl_3 but benzoic acid gives buff coloured precipitate.



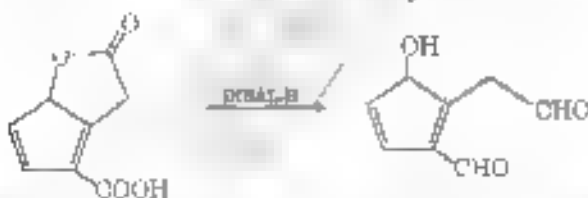
Competition File



- B41. a Since compound A molecular formula is C_8H_7Br , gives a light yellow ppt. when warmed with alcoholic $AgNO_3$, therefore, Br must be present in side chain. Therefore option b is wrong which Br is present in the ring is not possible. Further since the compound A gives an acid B, $C_8H_6O_4$ which readily forms an anhydride on heating, therefore, compound A must be α -disubstituted. Therefore, option (a) is correct.



- B46. (b) DIBAL-H reduces esters and carboxylic acids to aldehydes.



- B47. b Only aldehydes and ketones having CH_3CO -group give iodoform test. Therefore CH_3COCH_3 will react with sodium hypochlorite but CH_3CH_2CHO will not.

- B48. a The correct order of acid strength is α -toluic acid > benzoic acid > p -toluic acid.

- B49. d The compounds containing $C \equiv C$ group or $CH_3 - C(=O) - H$ group undergo iodoform reaction and form iodoform on

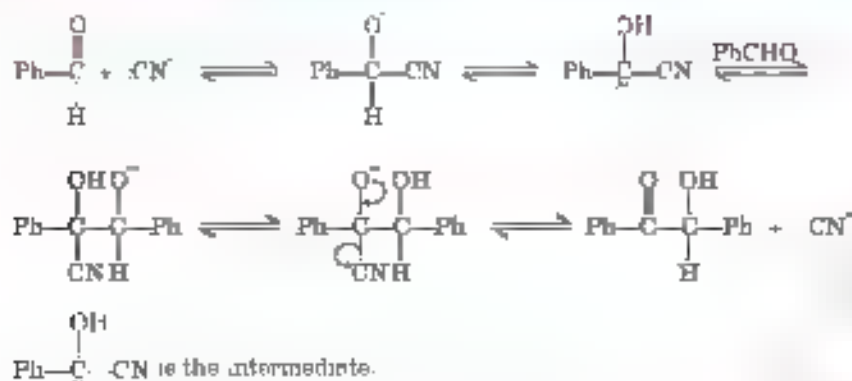
reaction with I_2 and aqueous $NaOH$. Therefore, $CH_3CH_2CH_2CH(OH)CH_3$ will give iodoform test.

- B50. (d) CH_3CHO because it has α -hydrogen.

- B51. b It is Clemmensen's reduction.

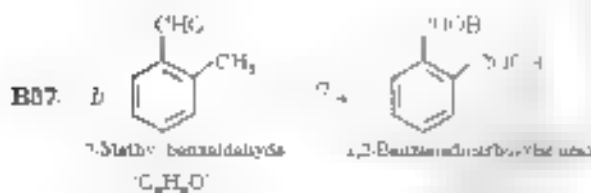
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B52. c. The mechanism for benzoin condensation is

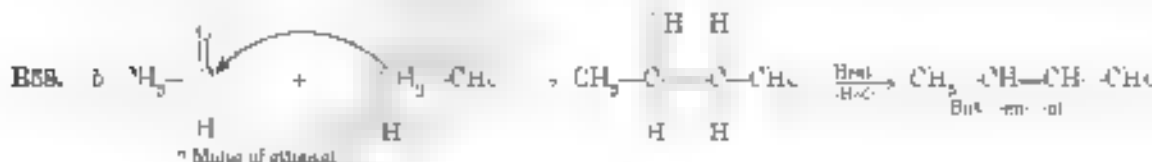


B53. (d) Reaction in acidic medium proceeds upto monobromination stage

B54. (c) Electron withdrawing group (NO_2) present in benzoic acid increases the acidic strength while electron releasing group (CH_3) decreases the acidic strength. Hence, correct order of acidic strength is IV < I < II < III.



This compound can react with Li^+ (NH_4^+) to form its derivative and reduces Tollen's reagent and undergoes Cannizzaro's reaction.



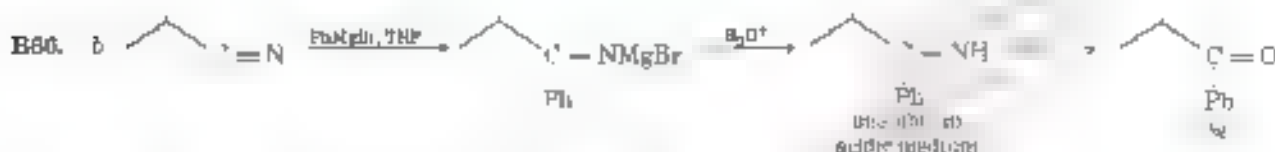
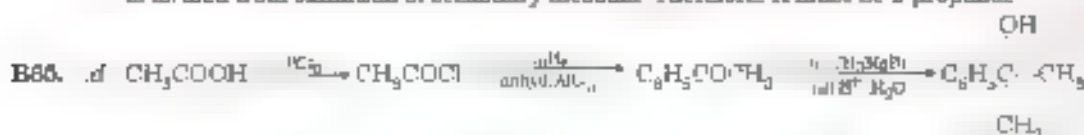
It is an intra-molecular Cannizzaro reaction.

B61. a In CCl_3CHO , there are three electron withdrawing chlorine groups attached to α -carbon. Therefore, it undergoes hydrolysis instead of Cannizzaro reaction.

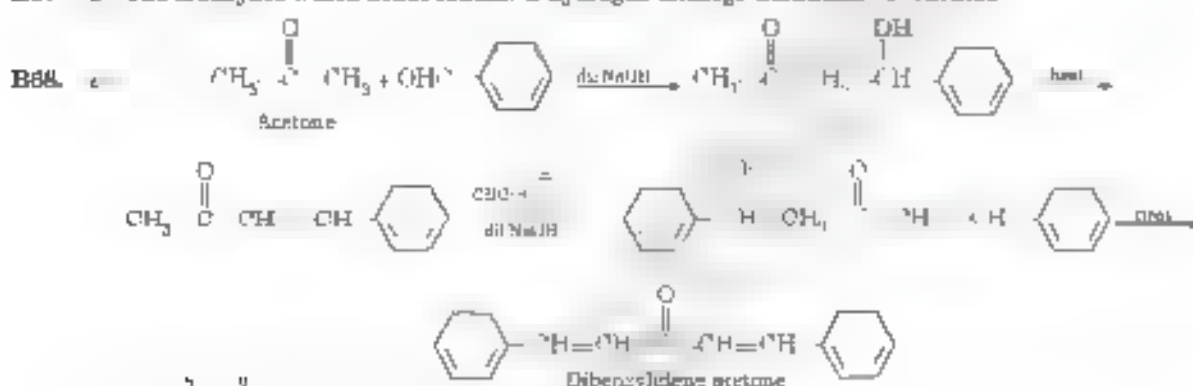
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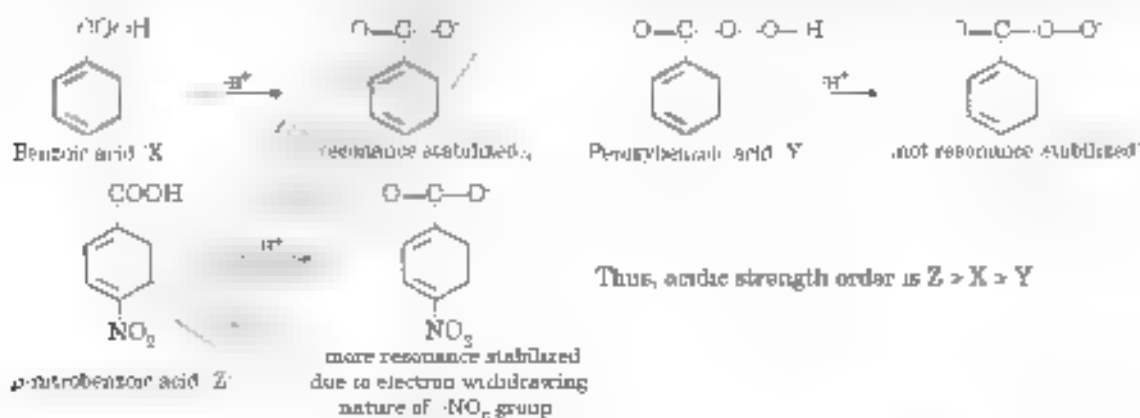
Product formed reacts with phenyl hydrazine but does not answer silver mirror test. Therefore, it must be a ketone. Ketone is formed from oxidation of secondary alcohols. Therefore, X must be 2-propanol.



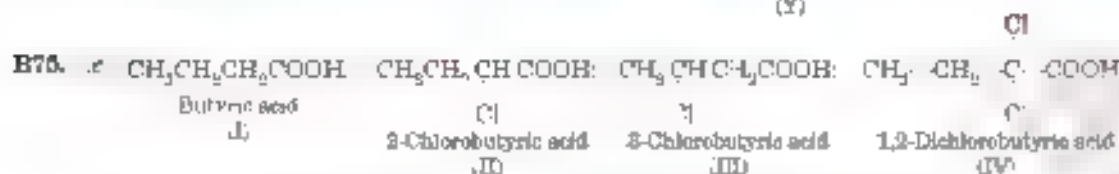
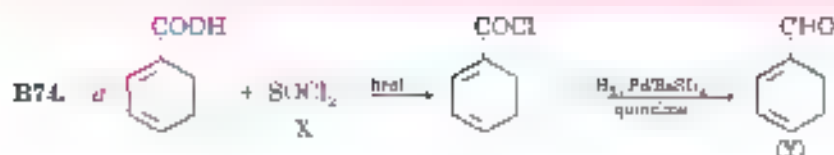
B67. b The aldehydes which do not contain α -hydrogen, undergo Cannizzaro's reaction.



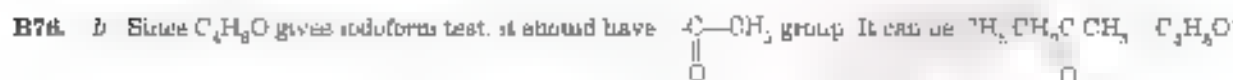
B70. c The acidic strength depends upon the stabilization of negative charge developed on anion. Due to loss of H^+ ion.



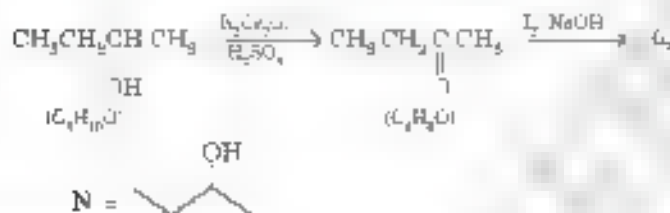
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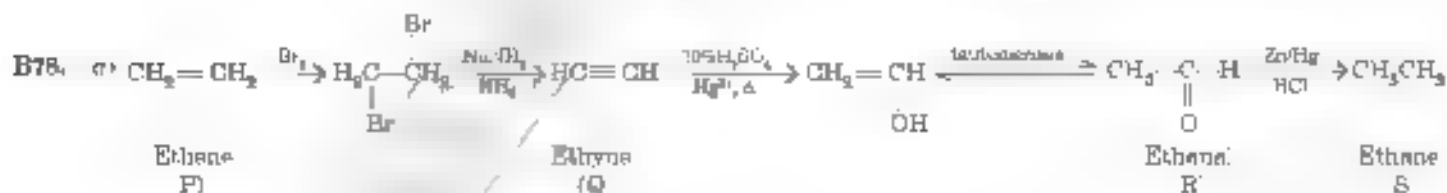
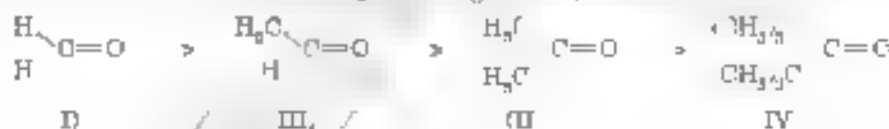
Electron withdrawing group (Cl) increases the acidic strength of carboxylic acid due to -I effect. The inductive effect decreases with increase in distance. Also, greater the number of such groups, larger is the acidic strength. Thus, order of increasing acidic strength is



Therefore, $\text{C}_4\text{H}_8\text{ON}$ should be $\text{CH}_3\text{CH}_2\text{CH}(\text{OH})\text{CH}_3$.



B77. a) With increase in steric hindrance, the tendency to undergo nucleophilic addition reaction decreases. So correct order is



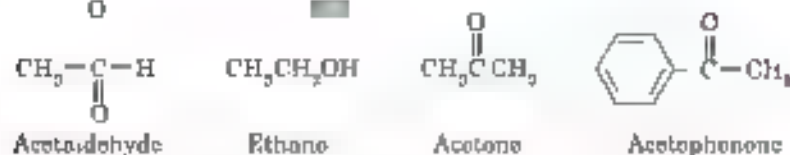
B79. a) The compounds having $\text{CH}_3-\text{C}(=\text{O})-$ or $\text{CH}_3\text{CH}_2-\text{C}(=\text{O})-$ undergo haloform reactions. Thus $\text{CH}_3\text{C}(=\text{O})\text{CH}_3$ undergoes haloform reaction.



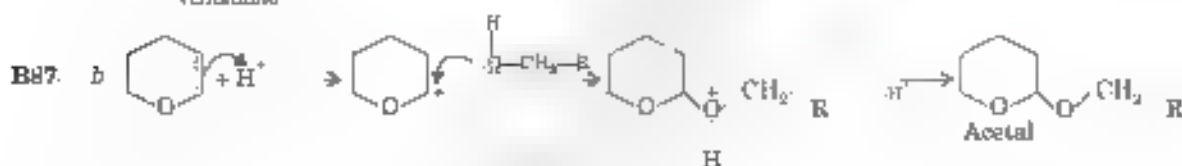
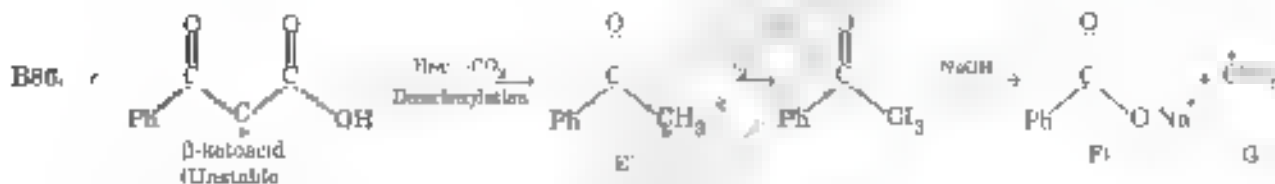
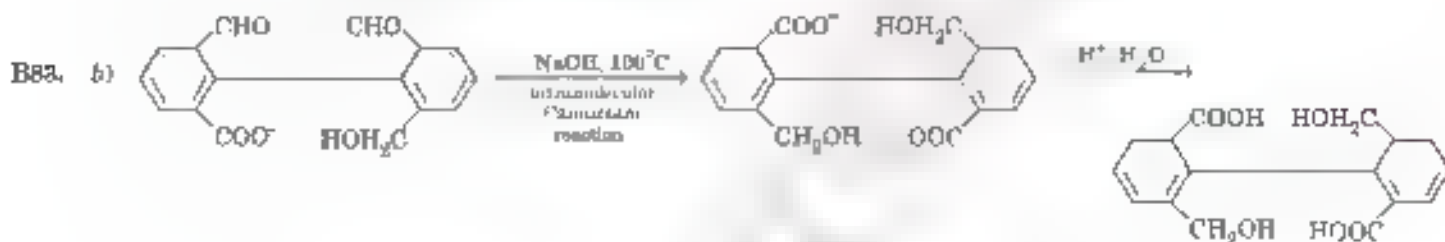
Both Zn-Hg, HCl and $\text{NH}_2\text{NH}_2, \text{KOH}$ can reduce $\text{C}(=\text{O})$ group to CH_2 group. But Zn-Hg, HCl will bring about substitution of OH group by Cl also. Therefore, most effective reagent is $\text{NH}_2\text{NH}_2, \text{KOH}$.

Competition File

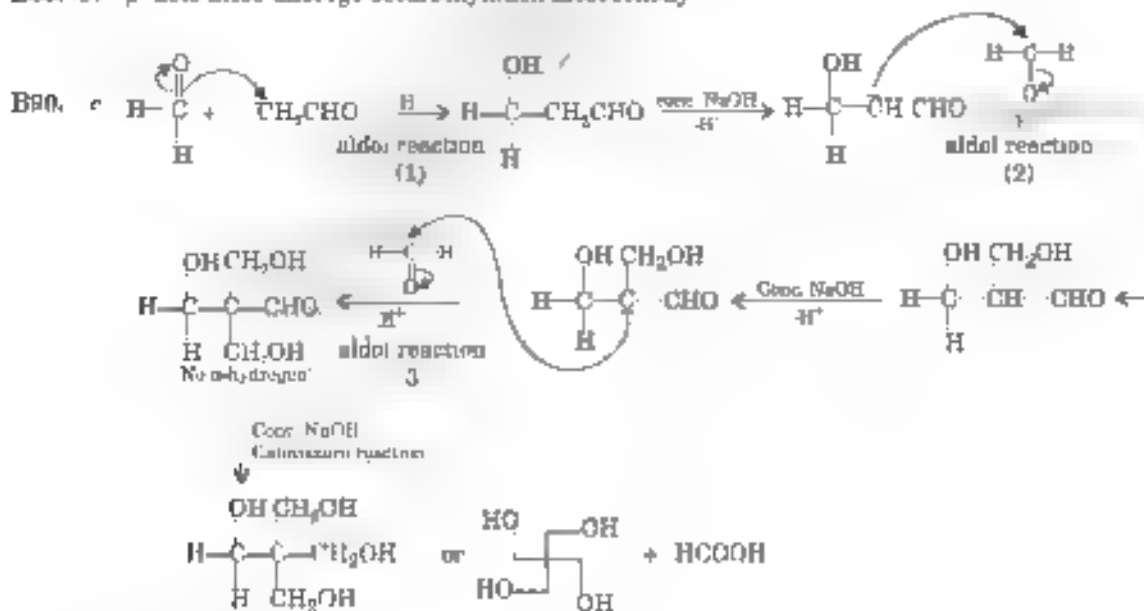
B81. (e) Haloform reaction is given by compounds containing



B82. (c) Ease of hydrolysis is acid halides > acid anhydrides > esters > amides



B88. (b) β -keto acids undergo decarboxylation most readily

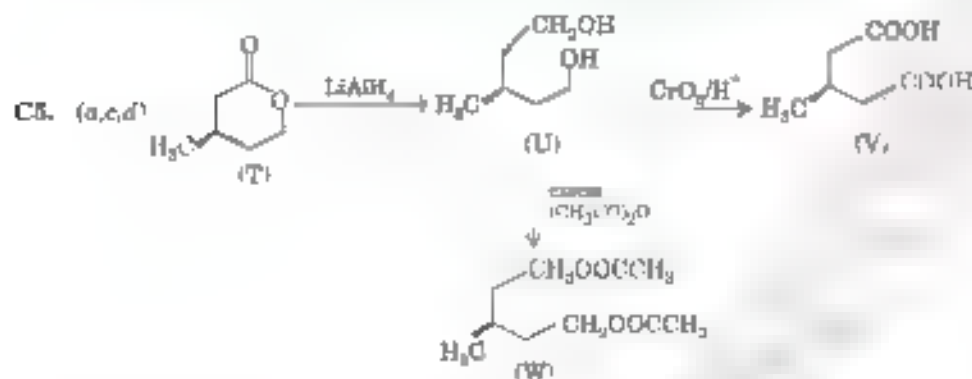


Competition File

C. mcq with more than one correct answer

C4. b, d

- a. C_6H_5OH and C_6H_5COOH can be separated by $NaHCO_3$ only and not by $NaOH$.
- b. C_6H_5COOH and $C_6H_5CH_2OH$ can be separated by both $NaHCO_3$ and $NaOH$ because in aq. $NaOH$ and $NaHCO_3$, C_6H_5COOH is soluble but $C_6H_5CH_2OH$ is insoluble.
- c. $C_6H_5CH_2OH$ and C_6H_5OH can be separated by only $NaOH$ and not by $NaHCO_3$.
- d. $C_6H_5CH_2OH$ and $C_6H_5CH_2COOH$ can be separated by $NaOH$ and $NaHCO_3$, because $C_6H_5CH_2COOH$ is soluble in $NaOH$ aq. as well as in $NaHCO_3$ (aq.) but $C_6H_5CH_2OH$ is not soluble.

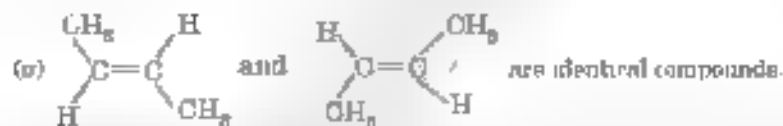


a) T is soluble in hot $NaOH$ /aq.

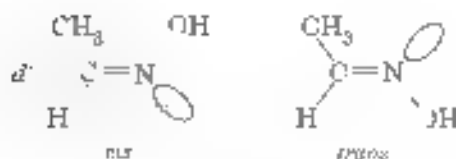
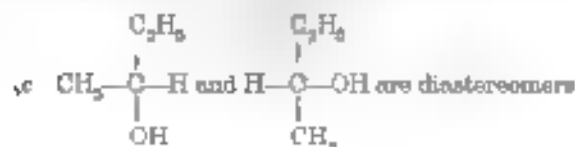


- c. Molecular formula of W is $C_{10}H_{18}O_4$.
- d. V gives effervescence on treatment with aqueous $NaHCO_3$ due to evolution of CO_2 .

C8. b, d

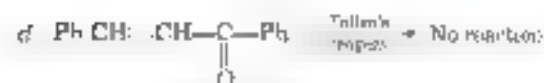
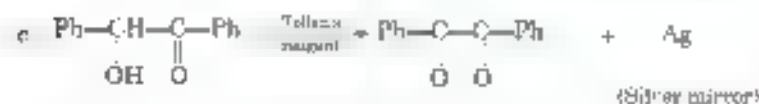
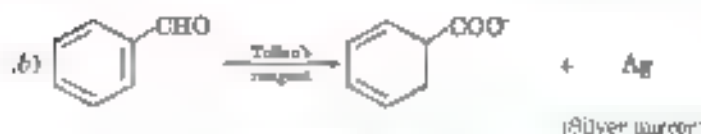
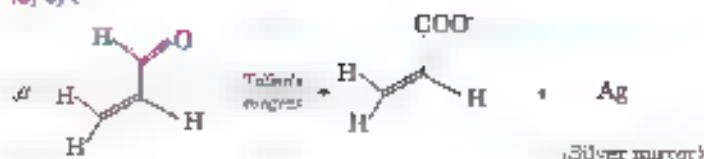


- b. CH_3CH on reaction with H_2N gives both dextrorotatory and levorotatory products resulting in formation of racemic mixture.



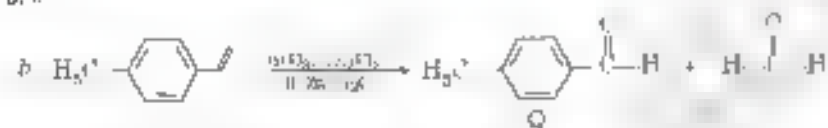
Competition File

C9. (a, b, c)

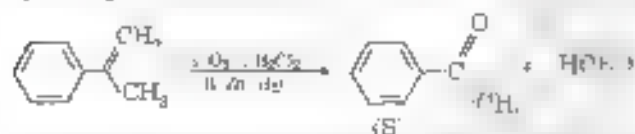


Tollens test is given by compounds having aldehyde group and α -hydroxy carbonyl compounds

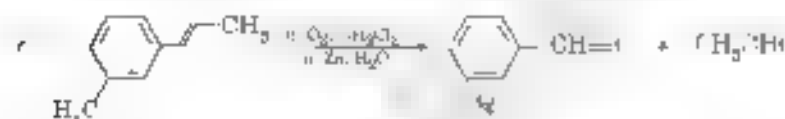
C10. (b, c)



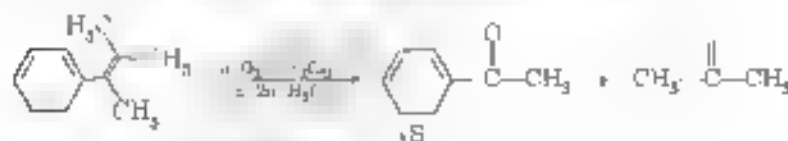
Q undergoes Cannizzaro reaction but not haloform reaction.



S undergoes haloform reaction but not Cannizzaro reaction.

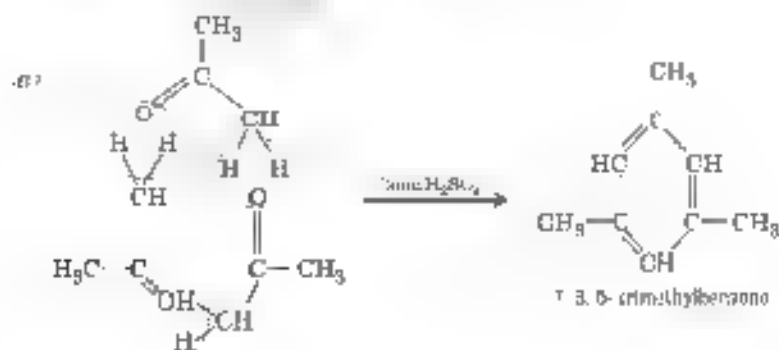


Q gives Cannizzaro reaction but not haloform reaction.

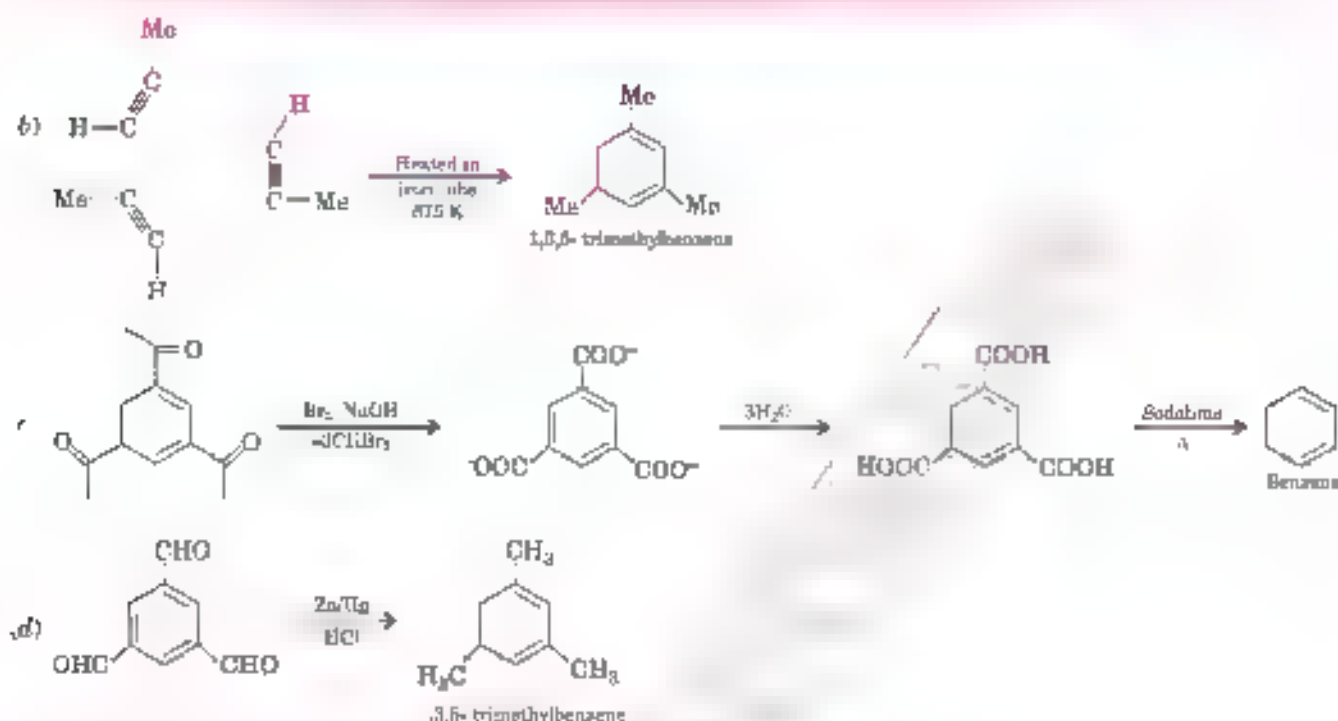


S gives haloform reaction but not Cannizzaro reaction.

C11. (a, b, d)

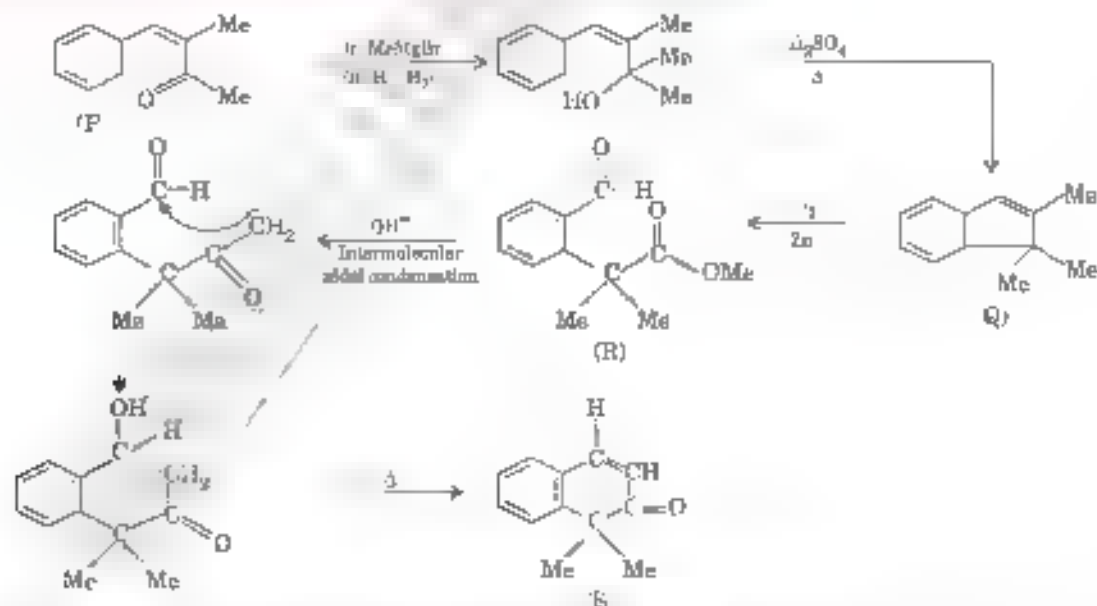


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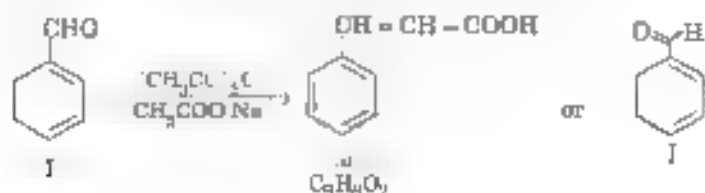


D mcq based on comprehension

D1. b D2. a D3. b Since 'P' gives positive iodoform test, it must be 2-methyl ketone

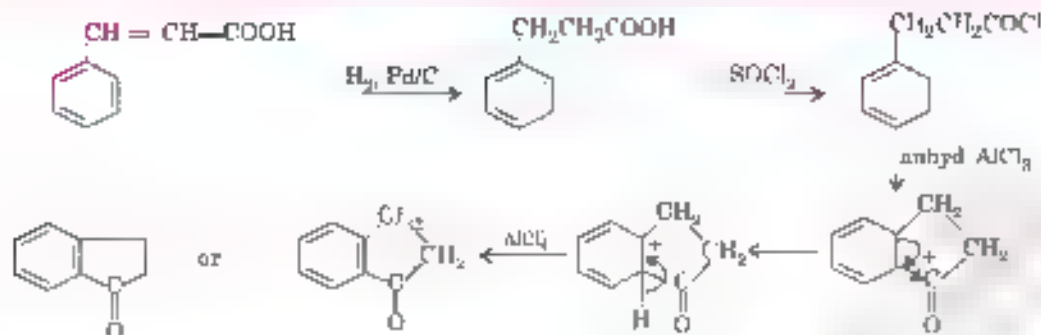


D4. a Since J gives effervescence on treatment with NaHCO_3 , it should contain COOH group. As it gives positive Baeyer's test, it should be unsaturated. J is obtained from I as

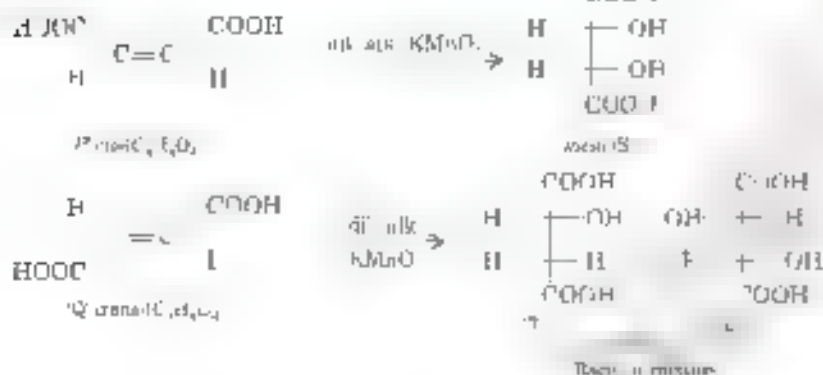


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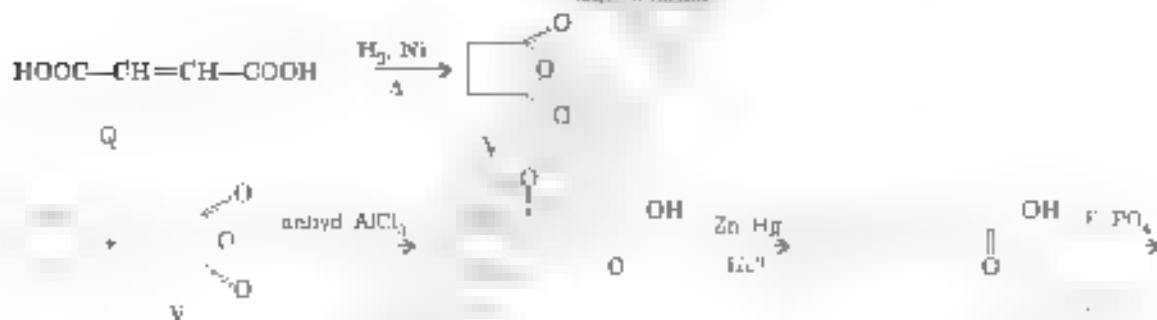
D5. (c)



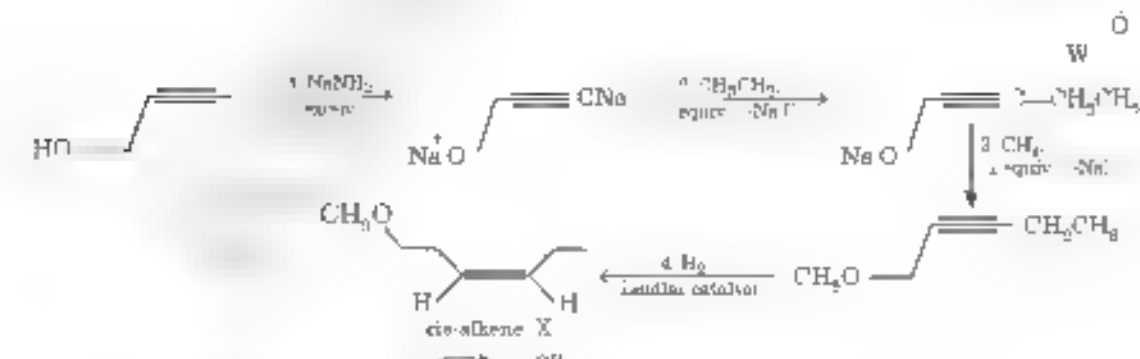
D6. (b)



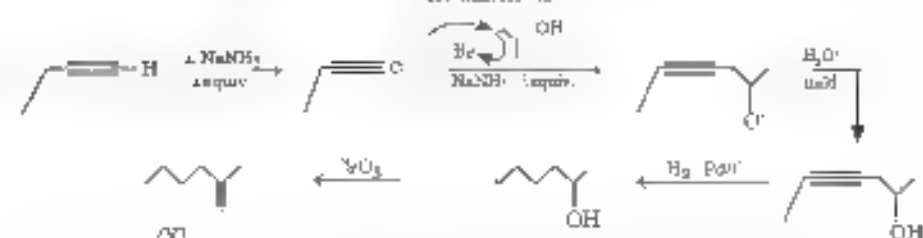
D7. (a)



D8. (c)

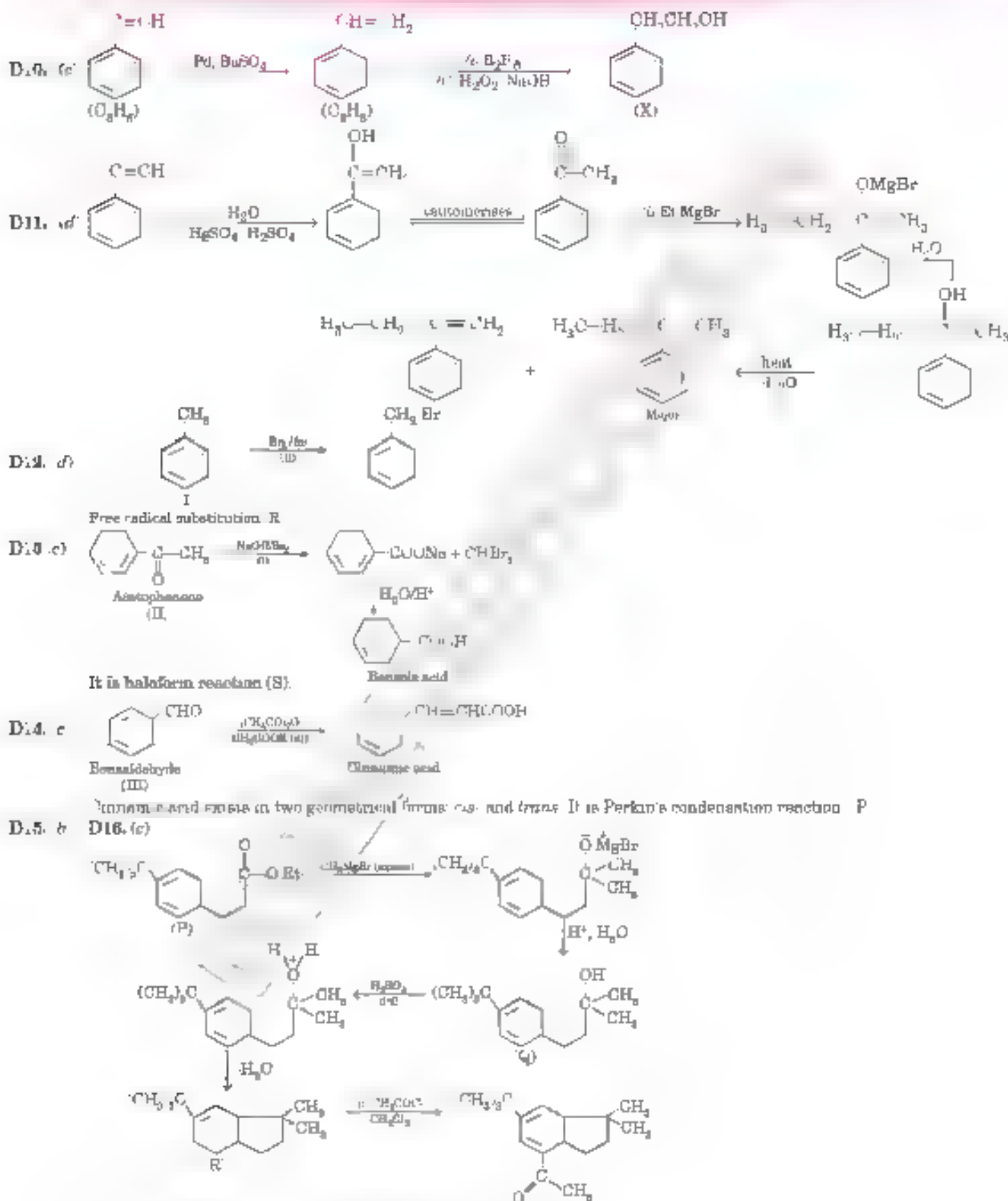


D9. (c)

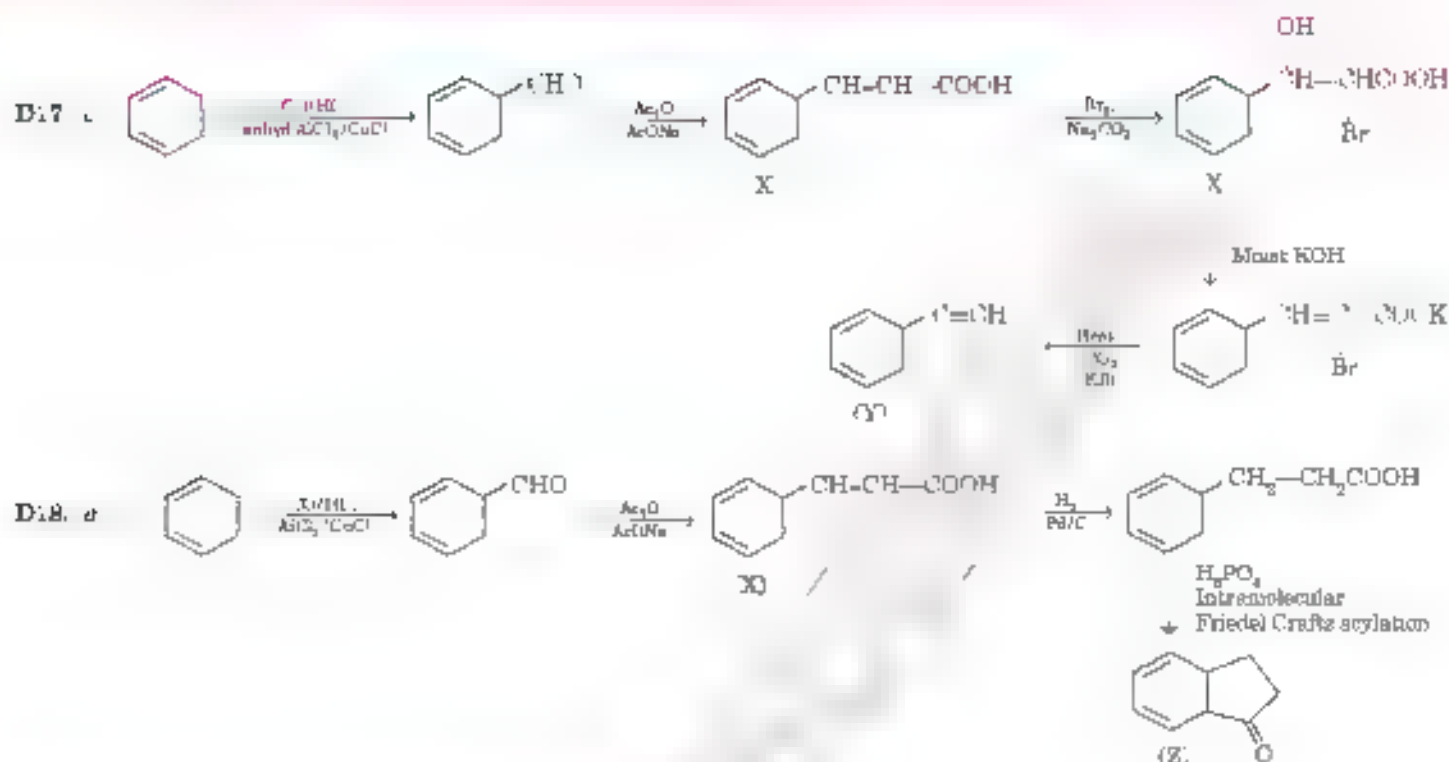


(X and Y) are functional isomers of each other and Y gives iodoform test.

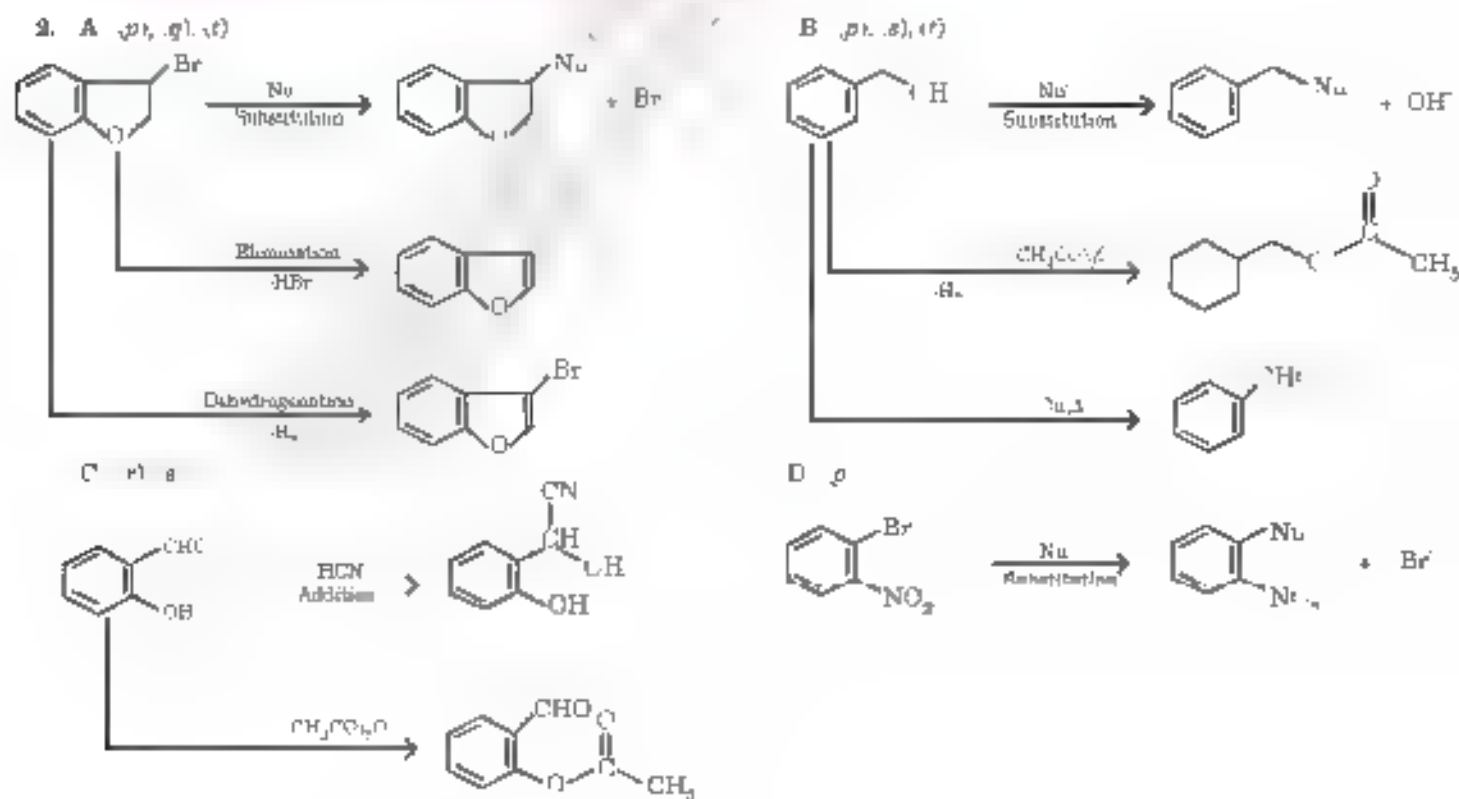
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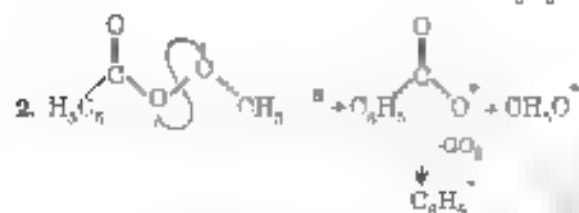
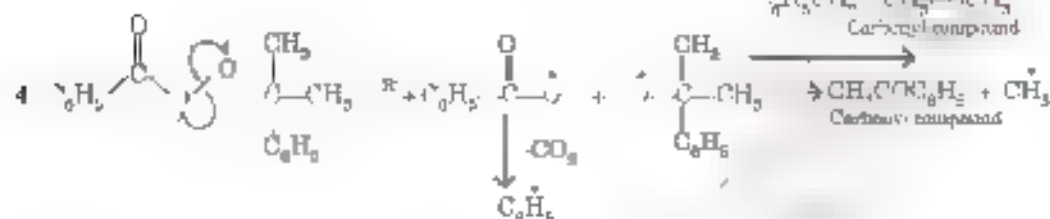
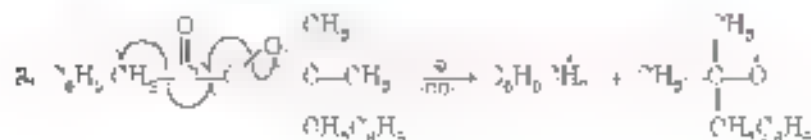


Matrix Match Type Questions

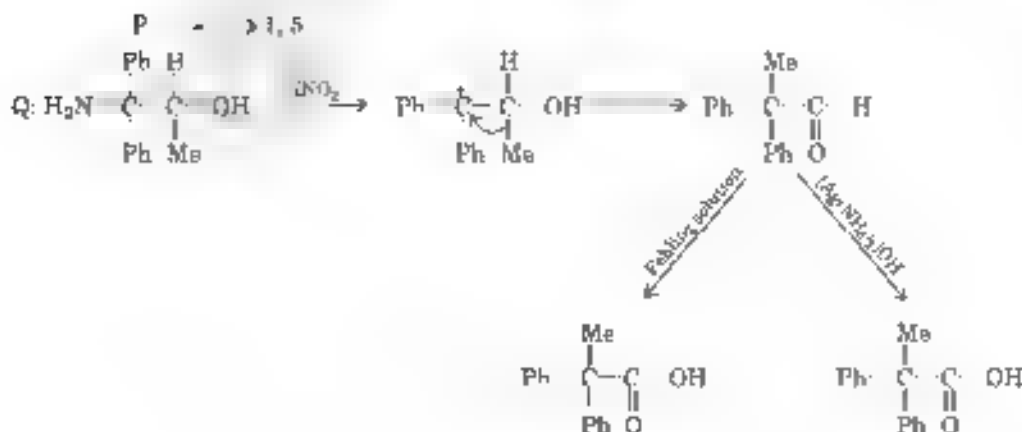
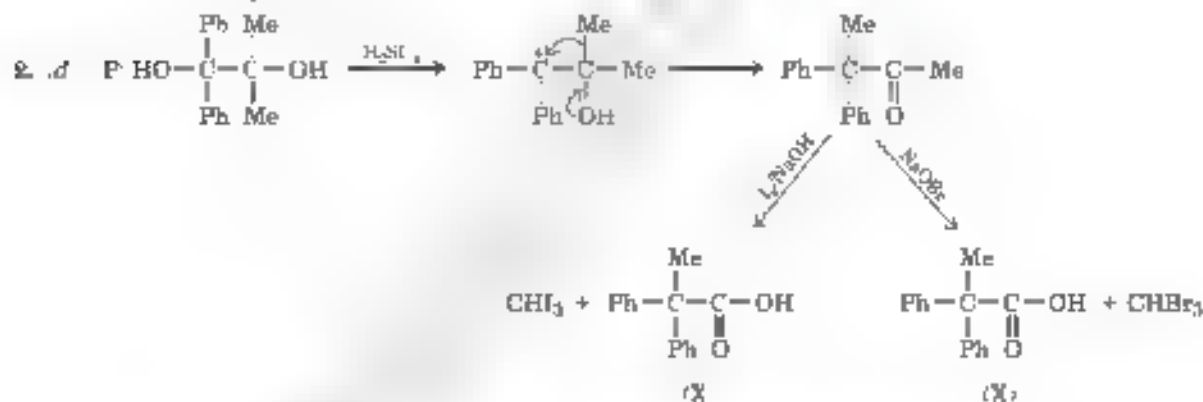


Competition File

Matching List Type Questions

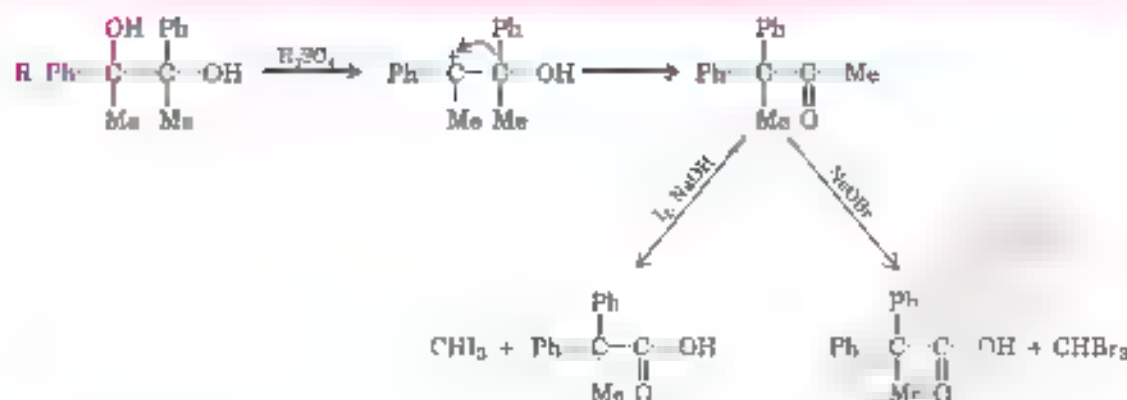


Thus, P 1 Q 3, R 4, S 2

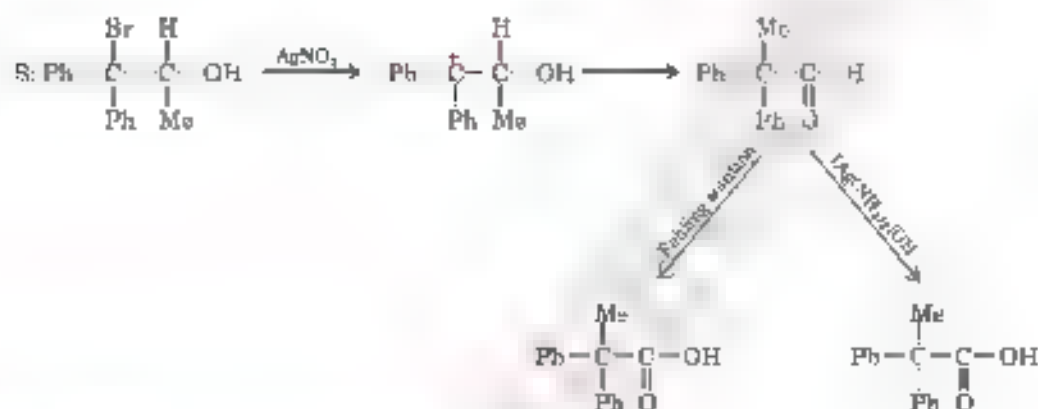


Q 2, 3

Competition File



R → 1, 5



S → 2, 3

Integer Type Questions

1. (4) Four isomers are possible



2. 5 2-methylpentanal, cyclohexan-1-one, 1-phenylpropanone, phenyl acetaldehyde and propanone contain α -hydrogen atoms and therefore undergo aldol condensation.
3. 4 $\text{CH}_3\text{COCH}_2\text{CH}_2\text{CH}_2\text{CH}_3, \text{CH}_3\text{COCH}(\text{CH}_3)\text{CH}_2\text{CH}_3, \text{CH}_3\text{CH}_2\text{COCH}_2\text{CH}_2\text{CH}_3$ and $\text{CH}_3\text{COCH}(\text{CH}_3)_2$ give iodoform test.
4. (3) Methanal, benzaldehyde, 2, 2-dimethylpropanal
5. (3) $\text{NH}_2\text{NH}_2, \text{KOH}, \text{HI}$ red P, $\text{Zn/Hg}, \text{HCl}$

6. (2) $\text{Ph}-\text{C}(=\text{O})-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$ does not react with Tollen's reagent.

7. (5) $\text{Ph}-\text{C}(=\text{O})-\text{CH}_2\text{CH}_3, \text{CH}_3\text{COCH}_2\text{CH}_2\text{CH}_2\text{CH}_3, \text{CH}_3\text{COCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}, \text{CH}_3\text{COCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CHO}$

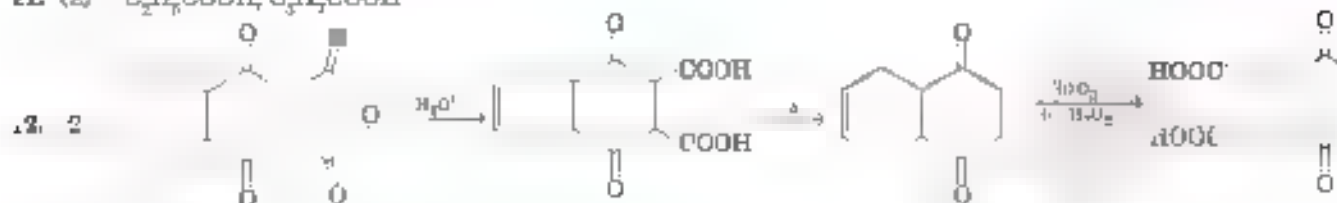
Competition File

8. 4 o-nitrobenzoic acid, p-chlorobenzoic acid, o-toluic acid, o-hydroxy benzoic acid

9. (7) All are more acidic than acetic acid

10. (8) $\text{COOH}-(\text{CH}_2)_3-\text{COOH}$

11. (2) $\text{C}_2\text{H}_5\text{COOH}$, $\text{C}_3\text{H}_7\text{COOH}$

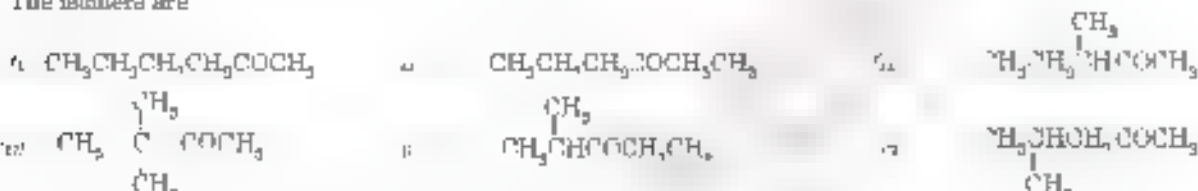


13. (5) General formula of ketones is $\text{C}_n\text{H}_{2n}\text{O}$

$$12 \times 1 + 2 \times n + 16 = 100 \text{ or } 2n = 84 \quad n = 42$$

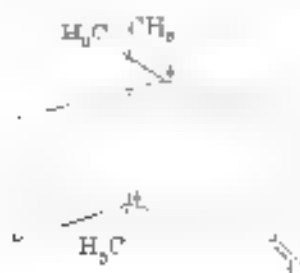
Hence ketone is $\text{C}_{42}\text{H}_{84}\text{O}$

The isomers are



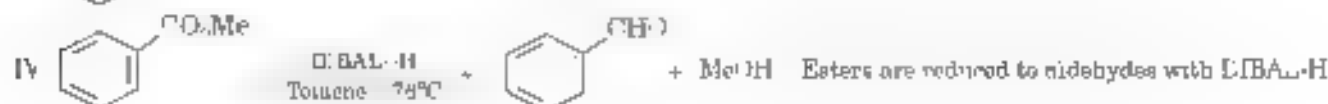
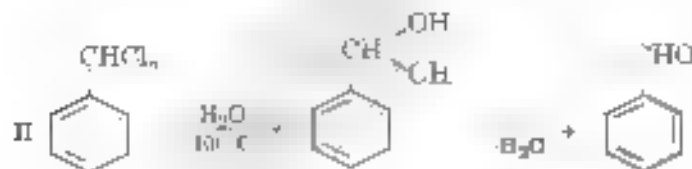
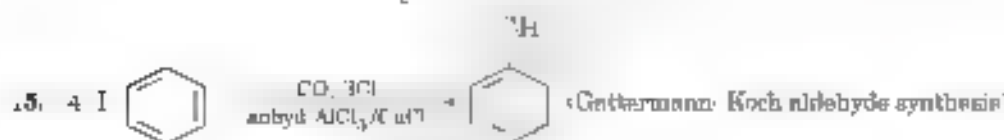
Only structure (iii), will not give racemic mixture on reaction with NaBH_4

14. (2) The compound has two chiral atoms therefore

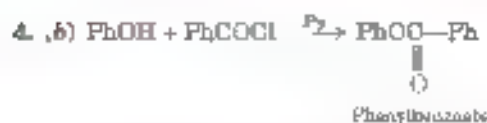
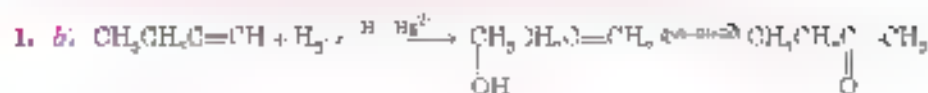


No. of stereoisomers = $2^2 = 4$

But due to bridging, rotation is not possible and only two optical isomers are possible: dextrorotatory and laevorotatory.



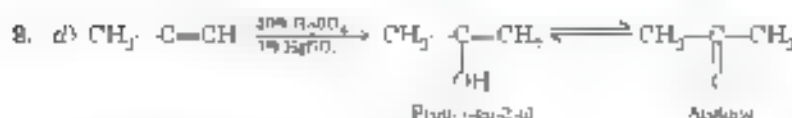
NCERT Exemplar Problems MCQs Type-I



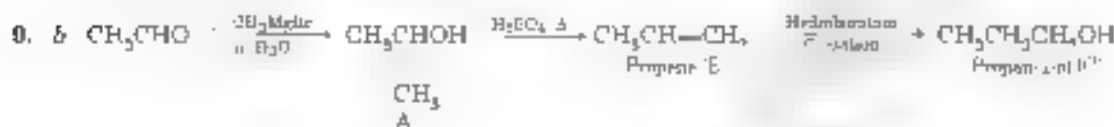
5. c) Fehling solution does not react with acetone and benzaldehyde

6. d) CH_3CHO does not undergo Cannizzaro's reaction because it contains α -hydrogen.

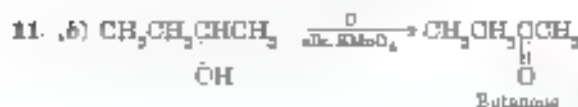
7. b



The isomerism is tautomerism

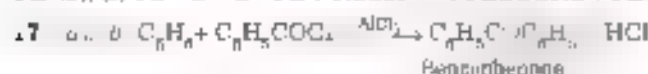
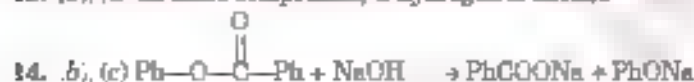


A and C are positional isomers.



NCERT Exemplar Problems, MCQs Type-II

12. b), d) In these compounds, α -hydrogen is absent.

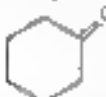
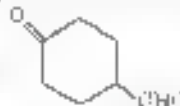


Unit Practice Test

for Board Examination

Time Allowed: 2 Hrs.

Maximum Marks: 95

- What type of hybridisation is involved for carbon in a carbonyl group? (1)
- Arrange the following compounds in the increasing order of boiling points
 $C_2H_5CO_2H$, $C_4H_9CO_2H$, $C_3H_7CO_2H$, $C_2H_5CO_2H$ (1)
- What is the name of the following reaction?
 $RCOCl + H_2 \xrightarrow{\text{anhyd. AlCl}_3} RCHO + HCl$ (1)
- Complete the reaction
 + $HCN \rightarrow ?$ (1)
- Draw the structures of hex-2-en-4-ynoic acid. (1)
- How will you convert the following to benzoic acid?
 Ethylbenzene (i) Bromobenzene (2)
- Write the structures of the products formed by the aldol condensation of the following
 2-Methylpentanal (i) Phenyl acetaldehyde (2)
- Explain the following
 Benzene acid is stronger acid than acetic acid
 Chloroacetic acid is stronger acid than acetic acid (2)
- Write the names of the reagents to bring about the following conversions:
 Ethane nitrile to ethane (i) *p*-Fluorotoluene to *p*-fluorobenzaldehyde (2)
- There are two $-NH_2$ groups in semicarbazide. However only one is involved in the formation of semicarbazone. Give reason. (2)
- Explain the following reactions by giving one example:
 Rosenmund reduction (i) Cannizzaro's reaction (ii) Wolff-Kishner reduction (3)
- Complete the following reactions
 $\xrightarrow[\text{Hydrolysis}]{H_2O, \text{boil}}$ (i) $C_6H_5CHO \xrightarrow{H_2NCONHNH_2}$ (8)
- Give one chemical test to distinguish between the following
 Pentan-2-one and pentan-3-one (i) Phenol and benzoic acid (2)
- Acetophenone and benzophenone (2)
- An organic compound A (molecular formula $C_5H_{10}O$) was hydrolysed with dilute sulphuric acid to give carboxylic acid B and an alcohol C. Condensation of C with chromic acid produced B. C on dehydration gives but-1-ene. Write equations for the reactions involved. (3)
- How will you convert acetic acid into
 acetamide (i) acetyl chloride (ii) ethyl acetate (3)
- (a) An organic compound with the molecular formula C_8H_8O forms 2,4-DNP derivative, reduces Tollen's reagent and undergoes Cannizzaro reaction. On vigorous oxidation, it gives 1,2-benzenedicarboxylic acid. Identify the compound.
 (b) Arrange the following compounds in the increasing order of their reactivity in nucleophilic addition reaction.
 Ethanal, propanal, propanone, butanone.
 (c) Although *p*-hydroxybenzoic acid is less acidic than benzoic acid, *ortho*-hydroxybenzoic acid is about 10^4 times more acidic than benzoic acid. Explain. (2, 1, 2)

► To check your performance, see HINTS AND SOLUTIONS TO SOME QUESTIONS at the end of Part II of the book.



UNIT 13

ORGANIC COMPOUNDS CONTAINING NITROGEN (Amino, Cyano and Diazo Compounds)

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Assessing

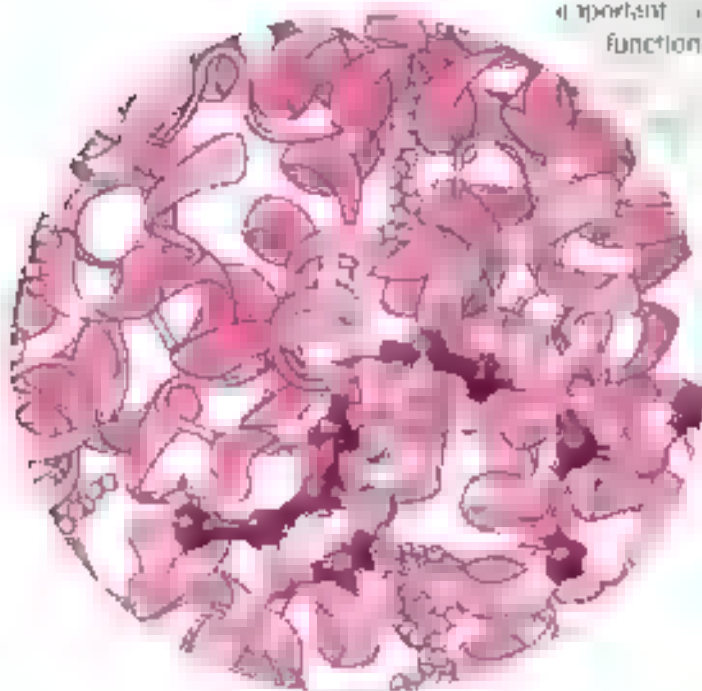
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Nitrogen is also an important constituent of many organic compounds. The important classes of organic compounds containing nitrogen as a part of functional group are

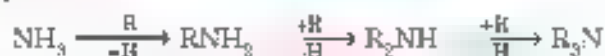


Functional group	Class of compounds	General formula
—NH—	(i) Primary amines	RNH—
—N—	(ii) Secondary amines	$\text{R}_2\text{NH—}$
—N—	(iii) Tertiary amines	$\text{R}_3\text{N—}$
$\text{—C}\equiv\text{N}$	Cyanides	$\text{RC}\equiv\text{N}$
$\text{—N}\equiv\text{C}$	Isocyanides	RNC
—NO_2	Nitro compounds	RNO_2
—O—N=O	Nitrites	RONO
$\text{—N}\equiv\text{N}^+\text{X}^-$	Diazonium salts	ArN_2^+X^-

PART A

AMINES

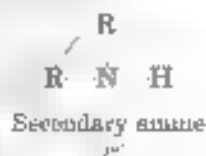
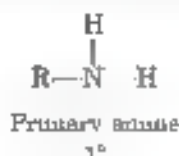
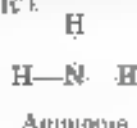
Amines are regarded as derivatives of ammonia in which one, two or all three hydrogen atoms are replaced by alkyl or aryl group.



Amines constitute an important class of organic compounds. They occur widely throughout both plants and animals. They are found among proteins, vitamins, alkaloids, hormones etc. Synthetic examples include polymers, drugs, dyestuffs etc. These amines find extensive uses. For example, **quinine** is an important antimalarial drug, **adrenaline** and **ephedrine** are used for increasing blood pressure, **novocain** is used as anaesthetic in dentistry, **codeine** is used as analgesic, pain killer, **benadryl** is used as antihistamine drug. Quaternary ammonium salts are used as surfactants.

CLASSIFICATION OF AMINES

The amines are classified as **primary (1°)**, **secondary (2°)** or **tertiary (3°)** according as one, two or three hydrogen atoms of ammonia in ammonia are replaced by alkyl or aryl groups, respectively. If one hydrogen atom of ammonia is replaced by alkyl (R) or aryl group (Ar), we get RNH_2 or ArNH_2 , a primary (1°) amine. If two H atoms of ammonia or one H atom of RNH_2 is replaced by another alkyl (R) or Ar group, we get R_2NH , which is a 2° amine. The second alkyl or aryl group may be same or different. Replacement of all the three H atoms of ammonia or another H atom of R_2NH by alkyl (R') or aryl group gives R_3N or $\text{R}_2\text{NR}'$ which is a 3° amine. R may be same or different, than R' or R''.

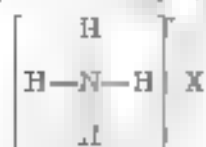


(where R, R' and R'' are alkyl groups).

The characteristic groups in primary, secondary and tertiary amines are



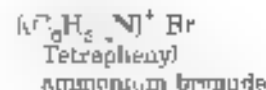
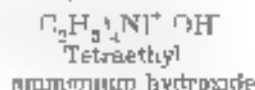
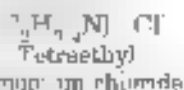
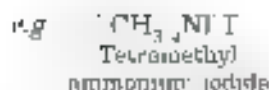
Apart from these three types of amines, there is another class of compounds known as **quaternary ammonium compounds**. These compounds may be regarded as derivatives of ammonium salts in which all the four H atoms are replaced by alkyl or aryl groups. For example,



Ammonium salt

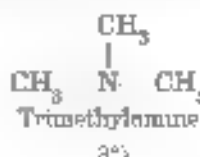
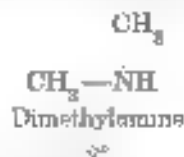


Tetraalkyl ammonium salt



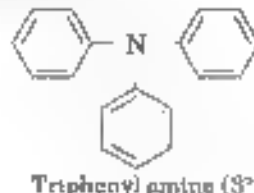
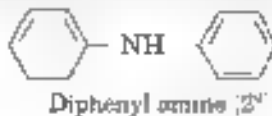
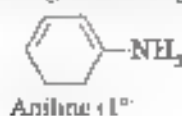
Amines may further be classified into two categories

1. Aliphatic amines: Amines in which the nitrogen atom is directly bonded to one or more alkyl groups are called **aliphatic amines**. For example,

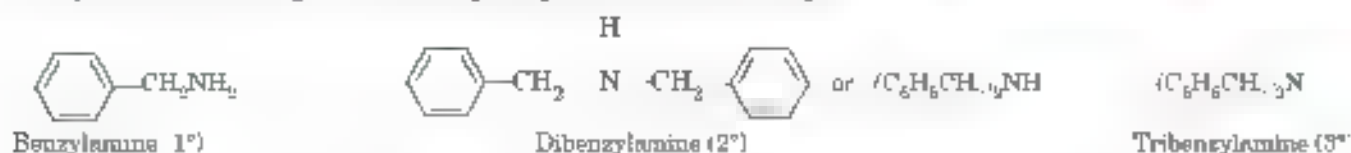


2. Aromatic amines: These are of two types

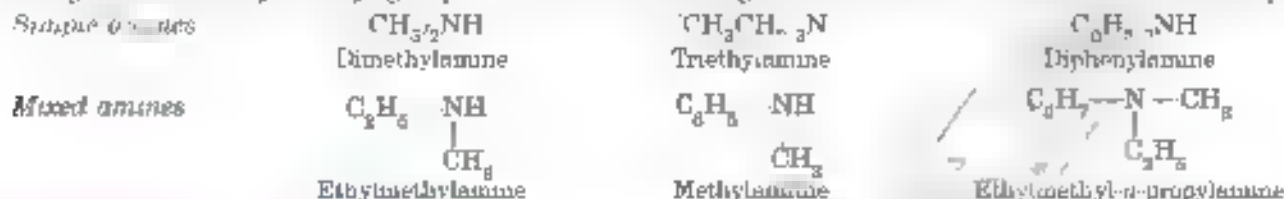
(a) Aryl amines. Amines in which the nitrogen atom is directly bonded to one or more (same or different) aromatic rings or aryl groups are called **aromatic amines**. For example,



(b) **Arylalkyl amines or side chain substituted amines.** Amines in which the nitrogen atom is bonded to the side chain of the aromatic ring are called **arylalkyl amines**. For example,



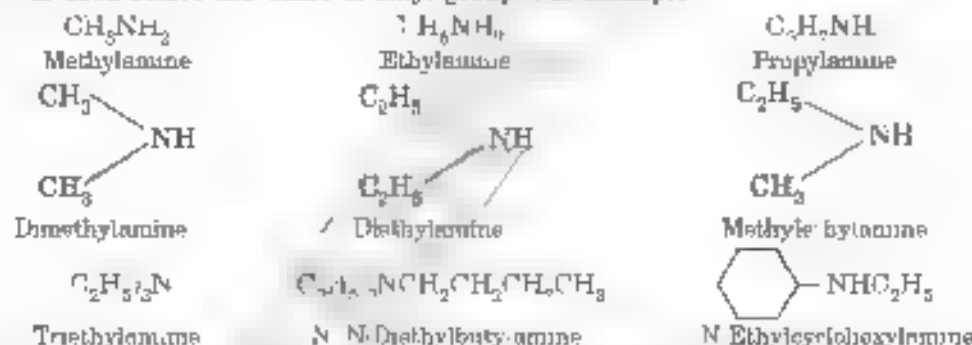
Simple and mixed amines. Secondary and tertiary amines may be classified as simple or mixed amines according as all the alkyl or aryl groups attached to the nitrogen atom are same or different. For example,



NOMENCLATURE OF AMINES

1. Aliphatic amines

Common names According to common system, amines are called **alkylamines** by adding the prefix amine to the name of the corresponding **alkyl groups**. In secondary and tertiary amines, when two or more groups are the same, the prefix *di* or *tri* is used before the name of alkyl group. For example

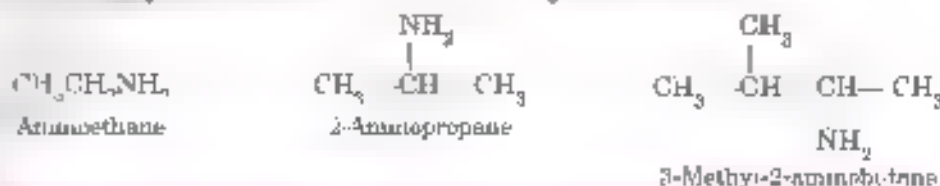


According to **second system**, primary amines are named as the **amino** (-NH_2) derivatives of the corresponding hydrocarbons and are called **aminoalkanes**. In this system, the primary amines are named by adding the **prefix amino** to the name of the parent alkane corresponding to the longest possible straight chain.

The position of the amino group and of the substituents, if any, are indicated by Arabic numerals. While numbering the chain, the carbon atom containing the amino group should get the lowest possible number.

The secondary and tertiary amines are named as *nitrogen substituted primary amines*, e.g. *N-alkylaminoalkanes*. While naming these, the word *N-alkyl* or *N,N-dialkyl* is prefixed to the word *amino alkane*. The prefixes *N* and *N,N* mean that the alkyl groups are attached to the nitrogen atom rather than to the carbon atom. It may be noted that if the two or three substituents are different, then the largest alkyl group forms the parent, *alkane amino alkane* and the smaller *alkyl* groups are regarded as substituents. For example

$\text{CH}_3\text{NHCH}_2\text{CH}_3$ is named as N-methylaminoethane and not as N-ethylaminomethane



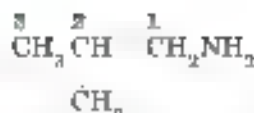
Note: Earlier this method was recommended by IUPAC. However, according to latest IUPAC³ recommendations this system is used only for naming amines which have a group of higher priority than -NH₂ group. For example



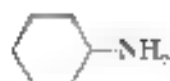
IUPAC names. In the latest IUPAC system, the aliphatic amines are also called **alkanamines**. These names are written by replacing 'e' of the name of parent alkane by suffix '**amine**'. For example, CH_3NH_2 may be named as **methanamine**. Similarly,



Ethanamine



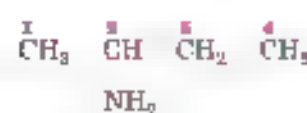
2-Methylpropan-1-amine



Cyclohexanamine

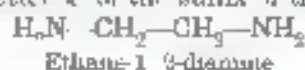


4,4-Dimethylcyclohexanamine

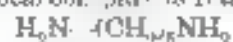


Butan-2-amine

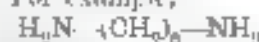
In case more than one amino group is present at different positions in the parent chain, their positions are specified by giving numbers to the carbon atom bearing NH_2 groups and suitable prefix such as *d*, *l* etc. is attached to the amine. The letter *e* of the suffix of the hydrocarbon part is retained. For example,



Ethane-1,2-diamine



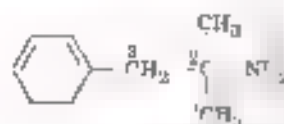
Pentane-1,5-diamine

Hexane-1,6-diamine
(Hexamethylenediamine)

It may be noted that in case of **aralkylamines**, the position of aryl group on the aliphatic carbon chain is indicated. For example,



Phenylmethanamine



2-Methyl-3-phenylpropan-3-amine

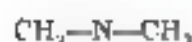
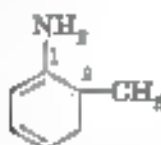
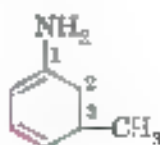
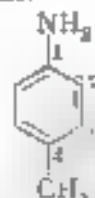
The common and IUPAC names of a few aliphatic amines and aralkyl amines are given below

Amine	Common name	IUPAC name
CH_3NH_2	Methylamine or Aminomethane	Methanamine
$\text{C}_2\text{H}_5\text{NH}_2$	Ethylamine or Aminomethane	Ethanamine
$\text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2$	n-Propylamine or 1-Aminopropane	Propan-1-amine
$\text{CH}_3\text{CH}(\text{CH}_3)\text{NH}_2$	Isopropylamine or 2-Aminopropane	Propan-2-amine
CH_3NHCH_3	N-Methylmethanamine or N-Methylaminomethane	N-Methylmethanamine
$\text{CH}_3\text{CH}_2\text{NHCH}_3$	Ethylmethanamine or N-Methylaminomethane	N-Methylethanamine
$\text{CH}_3\text{N}(\text{CH}_3)_2$	Trimethylamine or N,N-Dimethylmethanamine	N,N-Dimethylmethanamine
$\text{C}_2\text{H}_5\text{N}(\text{CH}_3)_2$	Ethyldimethylamine or N,N-Dimethylethanamine	N,N-Dimethylethanamine
$\text{CH}_3\text{CH}_2\text{N}(\text{CH}_3)_2$	Dimethylmethanamine or N-Ethyl-N-methylaminomethane	N-Ethyl-N-methylethanamine
$\text{CH}_3\text{CH}_2\text{N}(\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3)_2$	N,N-Diethylbutylamine	N,N-Diethylbutan-1-amine
Aralkylamines		
	Benzylamine or phenylaminomethane	Phenylmethanamine
	2-Phenylethanamine or 2-Phenylaminomethane	2-Phenylethanamine

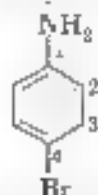
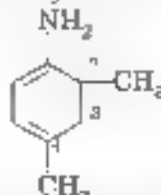
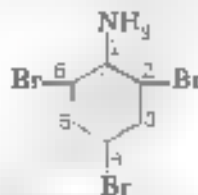
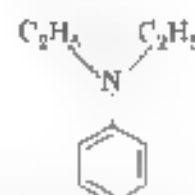
3. Aromatic amines

In common system, aromatic amines are called **aryl amines**. These are written by adding the suffix **amine** to the name of the aryl group. The simplest amine is $\text{C}_6\text{H}_5\text{NH}_2$ and it is known as **aniline**. It is also accepted IUPAC name. The other simple aromatic amines are named as **derivatives of aniline**.

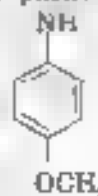
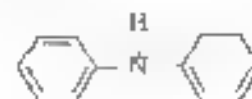
In the IUPAC system, the simplest aromatic amine $\text{C}_6\text{H}_5\text{NH}_2$ is called **benzenamine**. Other aromatic amines are named as derivatives of benzenamine and the positions of other groups are indicated by numbers. For example,

Benzeneamine
(Aniline)N-Methylbenzenamine
(N-Methylaniline)N,N-Dimethylbenzenamine
(N,N-Dimethylaniline)N-Ethyl-N-methylbenzenamine
(N-Ethyl-N-methylaniline)2-Methylbenzenamine
2-Methylaniline or o-Toluidine3-Methylbenzenamine
3-Methylaniline or m-Toluidine4-Methylbenzenamine
4-Methylaniline or p-Toluidine

In I.U.P.A. system benzenamine may also be written as aniline benzene

4-Bromobenzenamine
p-Bromoaniline2,4-Dimethylbenzenamine
2,4-Dimethylaniline2,4,6-Tribromobenzenamine
2,4,6-TribromoanilineN,N-Diethylbenzenamine
N,N-Diethylaniline

It may be noted that in some cases other names such as o/m/p-toluidine for o/m/p-methylaniline and o/m/p-aniline for o/m/p-methoxy aniline are assigned. Even Δ -phenyl derivative of aniline is generally called diphenylamine.

4-Methylbenzenamine
or 4-Methylaniline
(p-Toluidine)4-Methoxybenzenamine
or 4-Methoxyaniline
(p-Anisidine)N-Phenylbenzenamine
or N-Phenylaniline
(Diphenylamine)

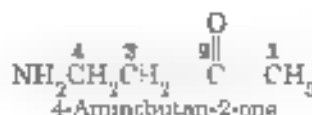
In case of poly functional groups, the amino group is considered as substituent and the other group constitutes the principal functional group and is preferred in getting lowest position. The compound is named as derivative of the principal functional group.

2-Aminobutan-4-ol
2-Aminobutan-4-ol

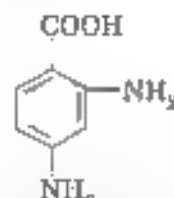
3-Aminopropan-1-ol



3-Aminopropanenitrile

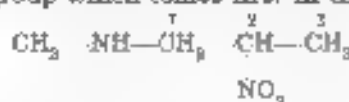
2-Aminobutan-4-ol
2-Aminobutan-4-ol

4-Aminobutan-2-one



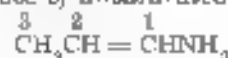
2,4-Diaminobenzoic acid

If however all the functional groups are substituent functional groups, the compound is named as a derivative of the compound containing the functional group which comes first in the alphabetical order

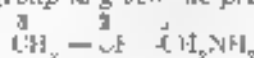


N-Methyl-2-nitropropanamine

In case of unsaturated amines, the amino group is given the preference. For example,

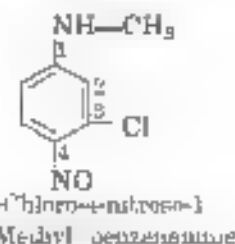
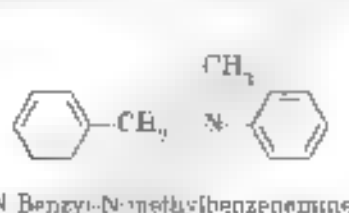
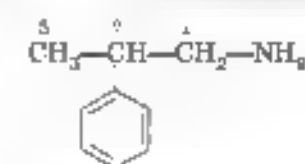
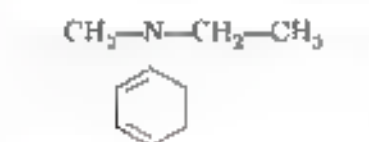
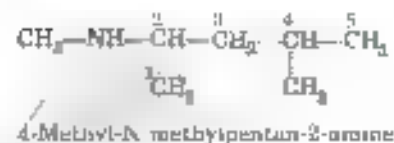
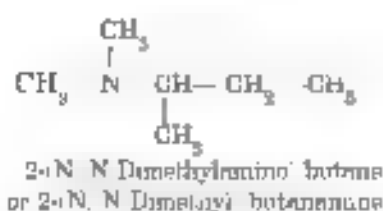
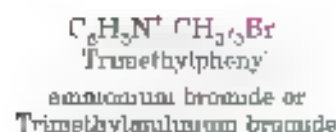
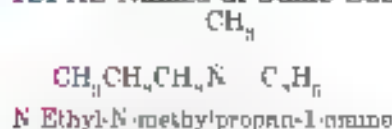


Prop-1-en-1-amine



Prop-2-en-1-amine allylamine

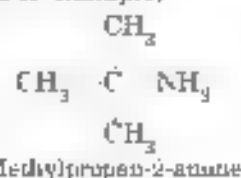
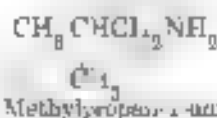
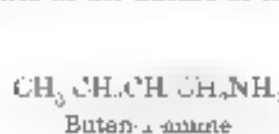
IUPAC Names of Some Complicated Amines



ISOMERISM IN AMINES

Amines exhibit the following types of isomerism

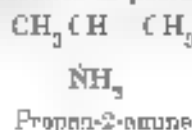
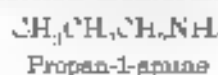
1. Chain isomerism. Aliphatic amines containing four or more carbon atoms show chain isomerism due to the difference in the nature of carbon chain of alkyl groups attached to the amino group. For example,



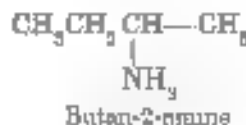
2. Metamerism. This is due to difference in the nature of alkyl groups attached to the same functional group. For example



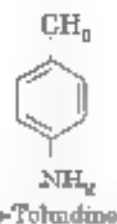
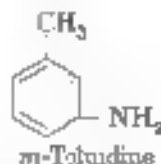
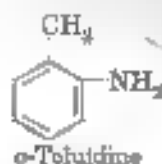
3. Position isomerism. This is due to the difference in position of amino group. For example,



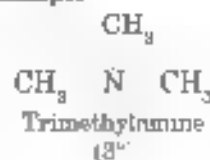
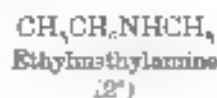
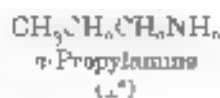
Similarly,



Aromatic amines also show position isomerism.



4. Functional isomerism. Primary, secondary and tertiary amines having the same molecular formula show functional isomerism among themselves because of the nature of amino groups. For example

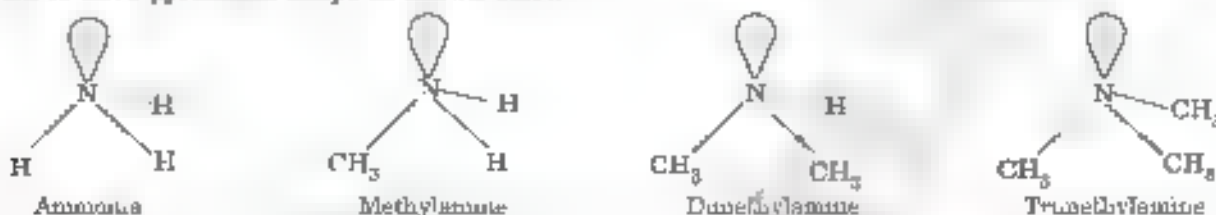


STRUCTURE OF AMINES

Amines are the derivatives of ammonia in which one or more hydrogen atoms have been replaced by alkyl or aryl groups. Therefore, the structures of amines are similar to ammonia. As we know, in ammonia nitrogen atom undergoes sp^3 hybridisation forming four sp^3 hybrid orbitals. Three of these sp^3 hybrid orbitals overlap with s -orbitals of H forming three N-H bonds. The fourth sp^3 hybrid orbital contains a lone pair of electrons.



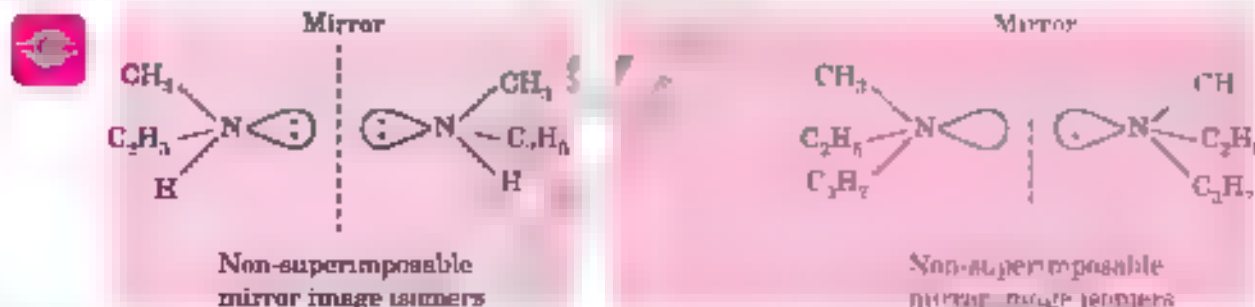
The geometry of the molecule is **pyramidal** and the bond angle in ammonia molecule is 107° . Since amines are derivative of ammonia in which one or more H atoms are replaced by alkyl or aryl groups, therefore, amines are also expected to have pyramidal shape as shown below.



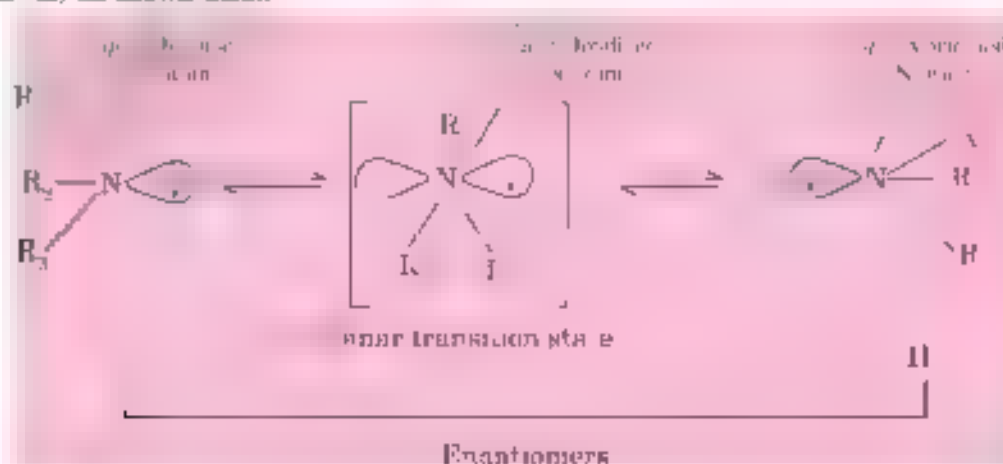
The bond angle in ammonia is 107° . However, due to the presence of methyl groups in amines, the bond angle increases. In case of 3° amine, due to steric hindrance between three bulky alkyl groups, bond angle increases from 107° in ammonia to 108° trimethylamine.

OPTICAL ACTIVITY OF AMINES

The aliphatic amines have pyramidal shape with one lone pair of electrons. Since in amines, N undergoes sp^3 hybridisation, the shape may be regarded as approximately tetrahedral when we assume electron pair on nitrogen as group. Therefore, the amines containing different n hydrogen atoms on nitrogen are **chiral** and we expect secondary and tertiary amines to exhibit optical activity or enantiomerism. For example, methyl ethylamine $\text{CH}_3\text{NHC}_2\text{H}_5$ a secondary amine or methyl ethyl propylamine (a tertiary amine) are dissymmetric as shown below.

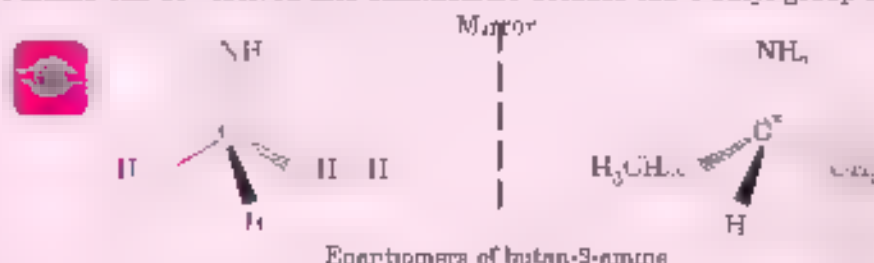


However, unlike chiral carbon compounds, most chiral amines cannot be resolved. This is because the two enantiomers rapidly interconvert into one another by a process called **nitrogen inversion** or **amine inversion**. This is known as **flipping**. This inversion which resembles an umbrella turning inside out, is very easy and occurs very rapidly (rate $\approx 1.3 \times 10^{10} \text{ s}^{-1}$). As a result of interconversion, it is very difficult to isolate a pure sample of either enantiomer. It has been observed that during nitrogen inversion, the state of hybridisation of N changes from sp^3 to sp^2 to give a planar transition state which can either revert to the starting amine or to its enantiomer (II) as shown below.



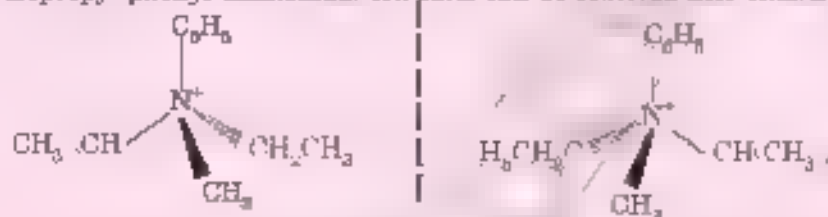
Although most simple amines cannot be resolved into enantiomers, the following types of chiral amines can be resolved.

1. **Amines whose chirality is due to the presence of asymmetric carbon atoms** can be resolved. For example, butan-2-amine can be resolved into enantiomers because the 2-butyl group is chiral.



Enantiomers of butan-2-amine

2. **Quaternary ammonium salts with asymmetric nitrogen atoms** can be resolved. The lone pair of electrons on the nitrogen atom is involved in nitrogen inversion and therefore, it is not possible to resolve the enantiomeric forms. However, if the lone pair of electrons on nitrogen is in a fourth different substituent, inversion of configuration is not possible. Therefore, quaternary ammonium salts exhibit optical activity. For example, methyl ethyl isopropyl phenyl ammonium ion salts can be resolved into enantiomers as



Enantiomers of methyl ethyl isopropyl phenyl ammonium ion

Similarly, N-oxides of tertiary amines having three different groups (R, R', R'') also show optical activity because of the absence of a lone pair of electrons on N which causes nitrogen inversion.

SOLVED EXAMPLES

Example 1.

Draw the structures, give names according to IUPAC and indicate primary, secondary and tertiary amines

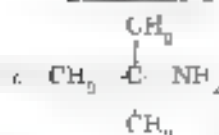
(a) eight isomeric amines of formula $C_4H_{11}N$

(b) five isomeric amines of formula C_7H_9N that contain a benzene ring

Solution: (a) Eight isomeric amines of formula $C_4H_{11}N$



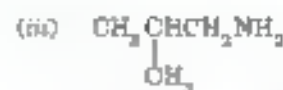
Butan-1-amine



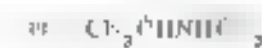
Butan-2-amine (1°)



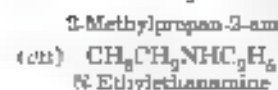
N-Methylpropan-1-amine (2°)



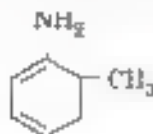
2-Methylpropan-1-amine (1°)



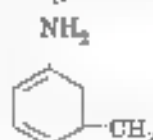
N-Methylpropan-2-amine (2°)



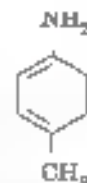
(b) Five isomeric amines of formula C_7H_9N containing a benzene ring



2-Methylbenzenamine
or 2-Methylaminobenzene
(1°)



3-Methylbenzenamine
or 3-Methylaminobenzene
(1°)

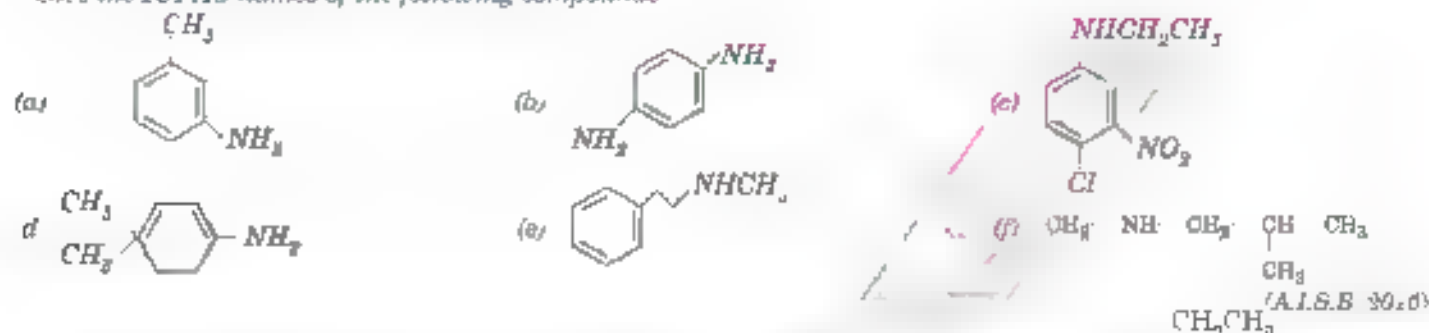


4-Methylbenzenamine
or 4-Methylaminobenzene
(1°)



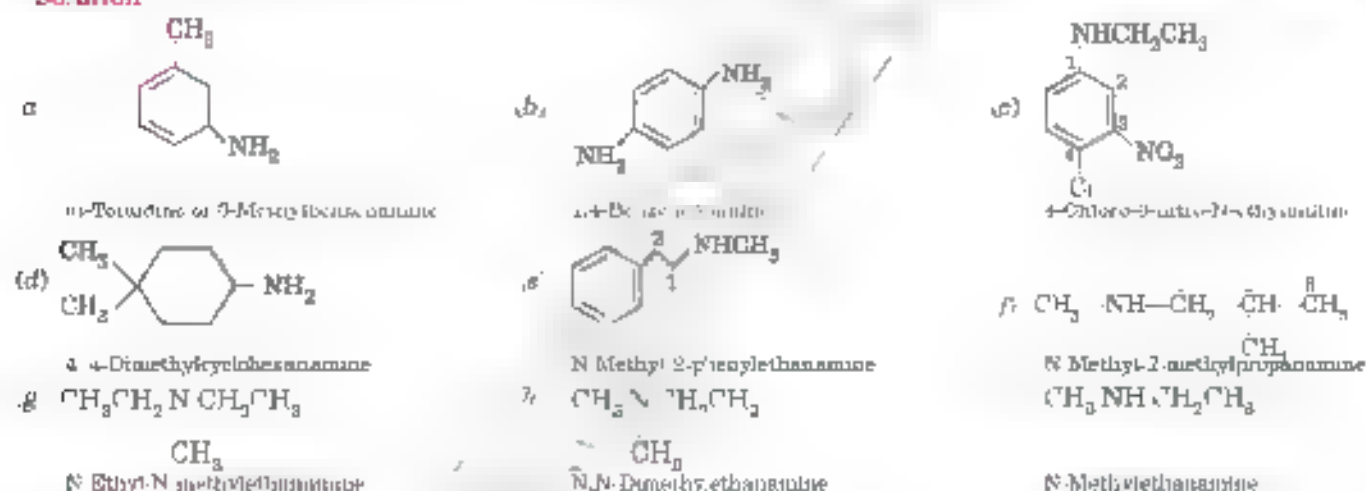
Example 2

Give the IUPAC names of the following compounds



g. $(\text{CH}_3\text{CH}_2)_2\text{NCH}_3$ I.S.B. 2017; H.S.B. 2018 h. $(\text{CH}_3)_2\text{NCH}_2\text{CH}_2$ I.S.B. 2017; J.S.B. 2017

Solution

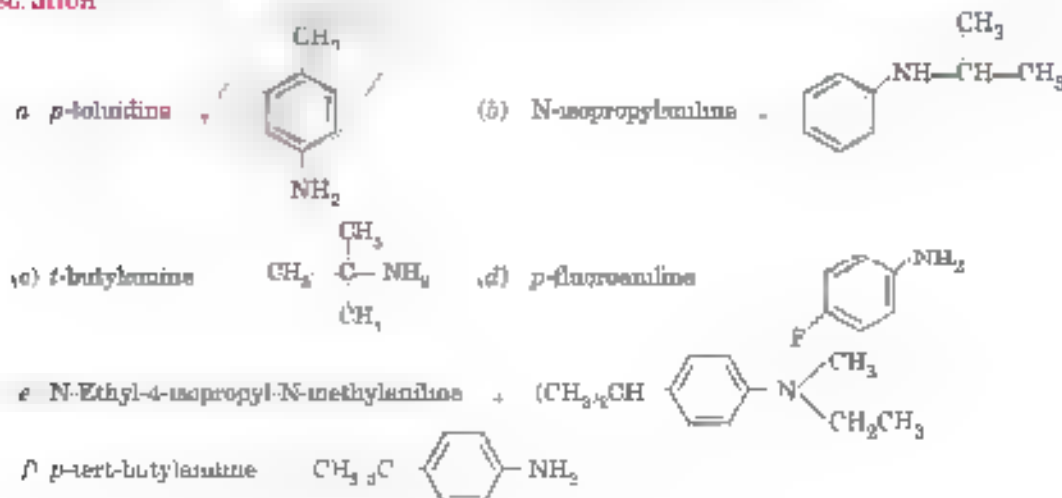


Example 3

Draw structures for the following compounds

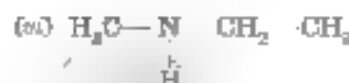
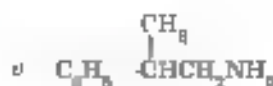
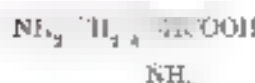
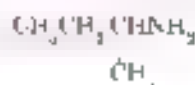
- (a) *p*-toluidine (b) *N*-isopropylaniline (c) *t*-butylamine
 (d) *p*-fluoroaniline (e) *N*-Ethyl-4-isopropyl-N-methylaniline (f) *p*-*tert*-butylaniline

Solution



Practice Problems

1. Write IUPAC names of the following



Karnataka S.B. P.O.Ja

• Ans.

Butan-2-amine

(a) 2-Diethylpropanamine

(b) 3-Phenylpropanamine

(c) 2,6-Diaminohexanoic acid

(c) 2-Phenylpropanamine

(d) N-Ethylethanamine

2. Write the structural formula of the following and indicate primary, secondary or tertiary amines

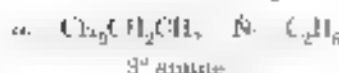
(i) N-Methyl butan-2-amine

(ii) 3-(N-Ethylamino) butan-1-ol

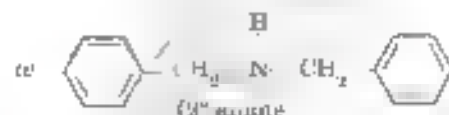
(iii) N-Ethyl-N-methylpropanamine

(iv) Dibenzylamine

• Ans.



3° amine



3. Predict which of the following names are not correct?

(i) N-Butylethanamine

(a) 1-Amino-2-ethanol

(c) Methylamine

(ii) Propanediamine

(b) 1-Phenylethanamine

• Ans. (i) The larger alkyl group should be considered as parent chain. Thus correct name is N-ethylbutanamine

(ii) -OH group should get preference. Correct name is 2-aminoethanol.

(iii) If methyl is bonded to amino N, it should be N-methylamine. If it is bonded to benzene ring, the correct name should be o-, m- or p-toluidine or 2-, 3- or 4-methylbenzenamine

(iv) The position of amino groups must be mentioned. It should be 1,2-propanediamine or 1,3-propanediamine

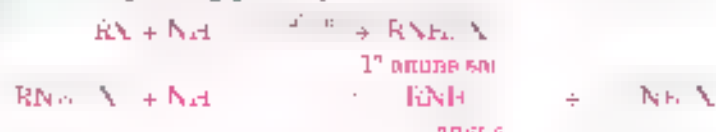
(v) It is correct

PREPARATION OF AMINES

The various methods for the preparation of amines are given below

1 From Alkyl halides

(a) By ammonolysis of alkyl halides **Hoffmann's ammonolysis method**. When an aqueous or alcoholic solution of ammonia is heated with an alkyl halide at 373 K in a sealed tube, all the three types of amines are obtained. In this reaction, the alkyl halides undergo **nucleophilic substitution reaction** in which the nucleophile ammonia or amine displaces the halogen atom. The ammonia molecule first attacks an alkyl halide molecule to form a primary amine salt. This salt then reacts with ammonia to give the corresponding primary amine and ammonium halide.



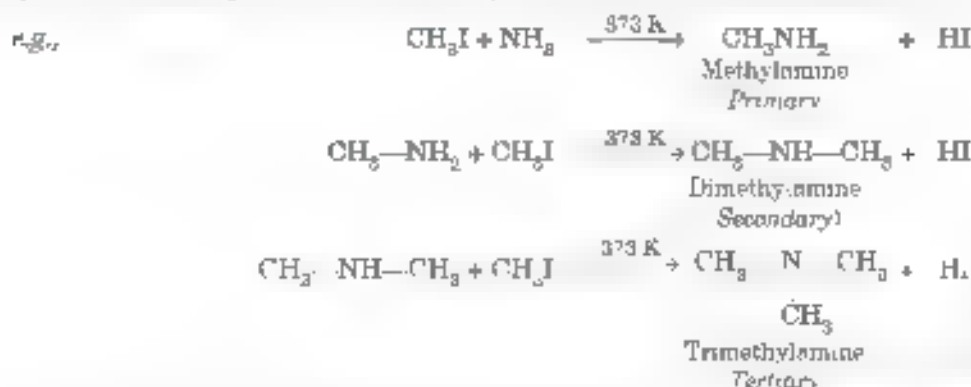
The free amine can also be obtained from the ammonium salt by treatment with a strong base



The primary amine also acts as a nucleophile and reacts further with alkyl halide and this sequence of reactions can lead to the formation of secondary, tertiary and finally quaternary ammonium salts.



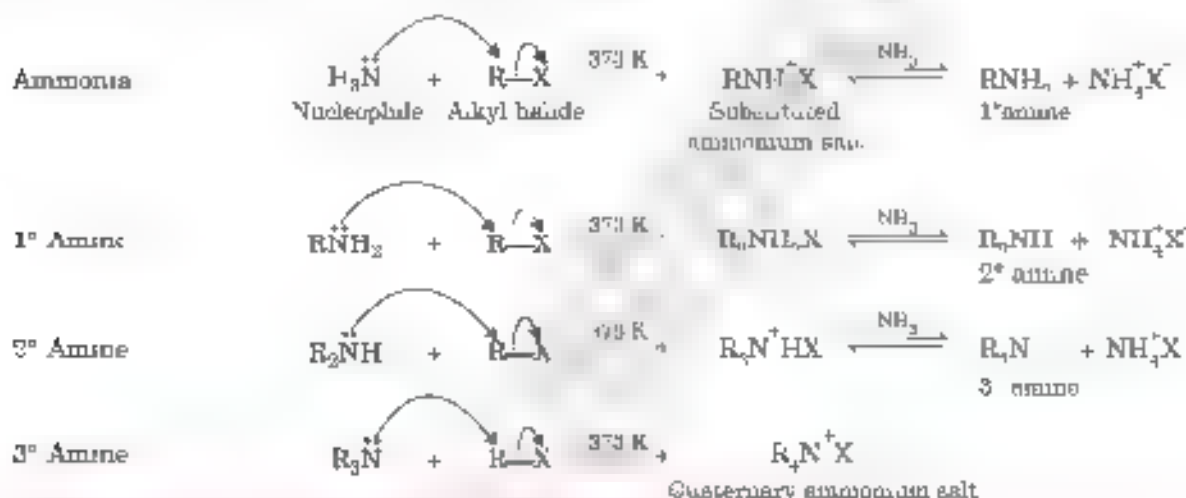
The process of cleavage of the C—X bond by ammonia or amines is called **Hoffmann's ammonolysis**.



Tertiary amines also combine with methyl iodide to form quaternary ammonium salts.



This reaction is an example of **nucleophilic substitution reaction** in which ammonia or amine molecule acts as a nucleophile due to the presence of lone pair on the nitrogen atom. The free amines are obtained from the substituted ammonium salts by treating with ammonia.



The order of reactivity of halides is **RI > RBr > RCl**

Benzyl halides also react with aqueous or alcoholic solution of ammonia to form benzyl amines.

Limitations. (a) This method gives a mixture of amines and it is very difficult to separate the mixture in the laboratory. However, the composition of the reaction mixture depends upon the amounts of alkyl halide and ammonia taken. There are two ways of getting only one product.

(i) **Using large excess of ammonia.** When ammonia is taken in a large excess in the reaction mixture, an alkyl halide is more likely to encounter and react with a molecule of ammonia rather than with a molecule of amine which is present in relatively much smaller amount. Therefore, only primary amine is formed as the main product.

(ii) **Using a large excess of alkyl halide.** Under these conditions in the presence of a base which will consume HX formed, quaternary ammonium salt is the main product.

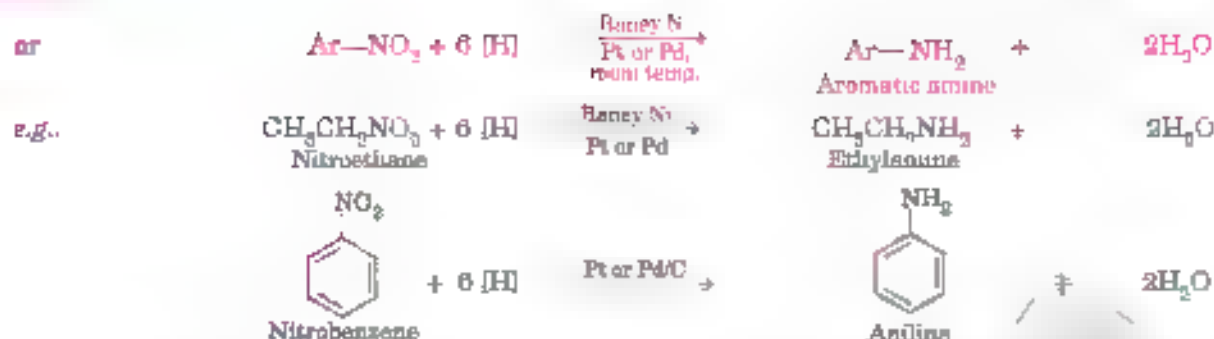
(b) The method is not suitable for the preparation of aryl amines because aryl halides are relatively very less reactive than alkyl halides towards nucleophilic substitution reactions.

2. Reduction of nitro compounds

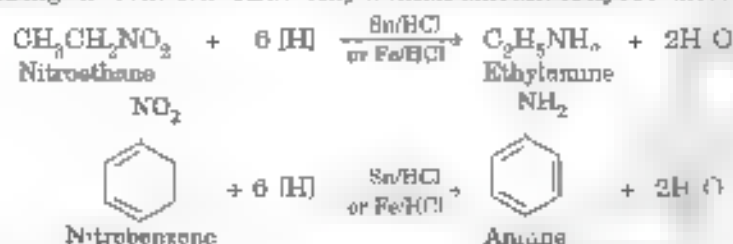
Aliphatic and aromatic amines can be easily prepared by the reduction of corresponding nitro compounds. The reduction can be carried out in a number of ways as discussed below.

(a) **Nitro compounds can be catalytically reduced** by passing hydrogen gas in the presence of Raney Ni, finely divided platinum or palladium as catalyst at room temperature.





(b) Nitro compounds can be reduced with **active metals** such as Fe, Sn, Zn or **aqueous hydrochloric acid**. Reduction with iron scrap and hydrochloric acid is preferred because FeCl_3 formed gets hydrolysed to release hydrochloric acid during the reaction. Thus, only a small amount of hydrochloric acid is needed to initiate the reaction.



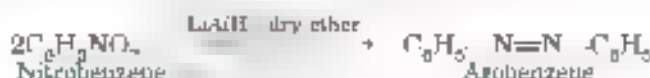
A mixture of SnCl_4 and conc. HCl has also been used for the reduction of aromatic nitro compounds.

This is a good method for the preparation of aromatic amines because these cannot be prepared from the corresponding aryl halides on treatment with ammonia. The required nitro compounds can be easily prepared by the nitration of arenes.

(c) Nitro compounds can also be reduced to amines with lithium aluminium hydride, LiAlH_4 .

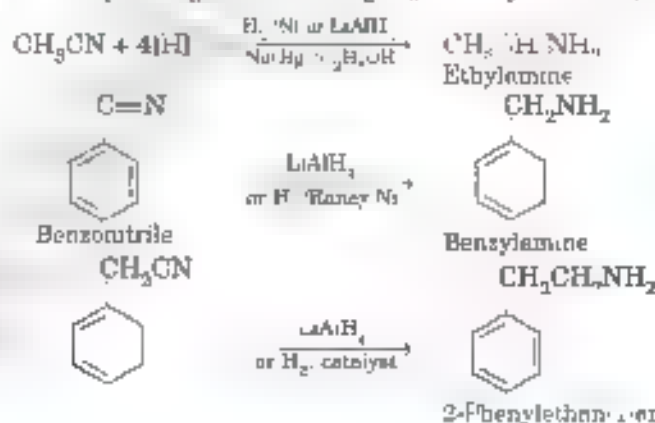


However, reduction of aromatic nitro compounds with LiAlH_4 gives azo compounds and not primary amines.



3. Reduction of nitriles, cyanides and isocyanides (isocyanides)

Nitriles can be reduced to corresponding amines using H_2 , Raney Ni or Pt, LiAlH_4 or NaBH_4 , $\text{C}_2\text{H}_5\text{OH}$.



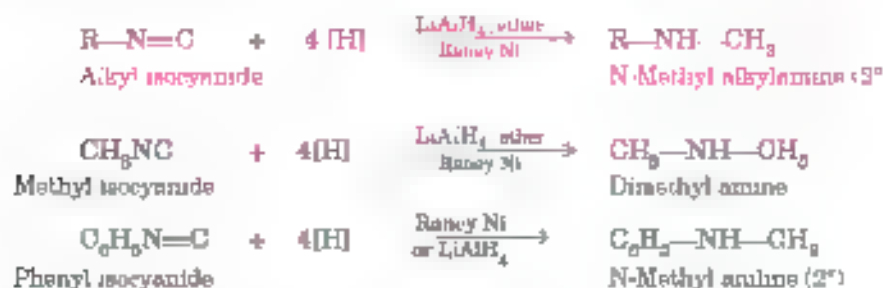
The method of reduction of cyanide with sodium and alcohol is called **Mendius reaction**.

HELP

Synthetic Importance: This reaction is very important for **ascend of amines series**. This is because alkyl nitriles can be readily prepared by the action of alcoholic NaCN or KCN on alkyl halides. The method can be used to prepare primary amines having one carbon more than the parent alkyl halide.



The reduction of isocyanides under similar conditions gives secondary amines i.e. N-alkyl amines.

**NOTE**

This method can be used only for the preparation of 2^o amines in which one of the alkyl groups is always methyl.

4. Reduction of amides

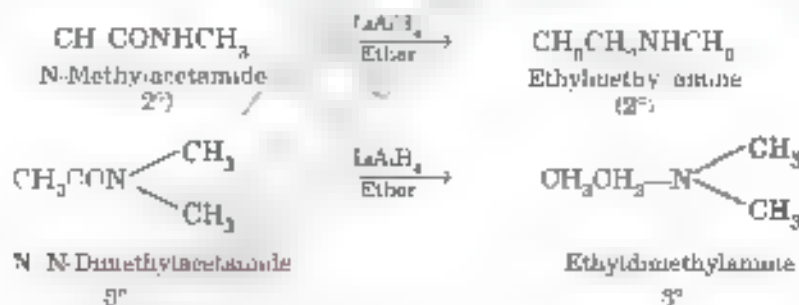
Amides are reduced to the corresponding amines by LiAlH_4 or $\text{Na/C}_2\text{H}_5\text{OH}$. Primary, secondary or tertiary amines can be prepared by this method by the reduction of corresponding amides.



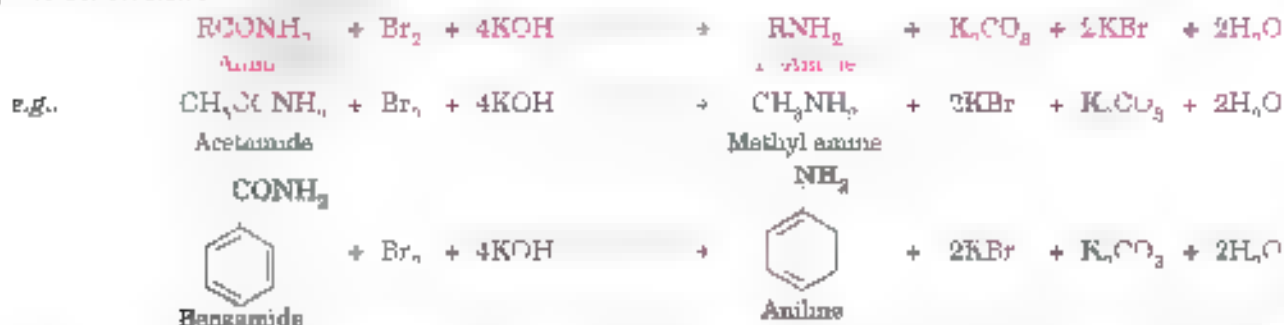
It is to be noted that the product contains one atom less of carbon atom than the original amide.



Secondary and tertiary amines can be prepared by the reduction of secondary and tertiary amides respectively.

**5. Hoffmann's bromamide degradation method**

Primary amines can be prepared from amides by treatment with Br_2 and KOH or NaOH . The amine formed contains one carbon atom less than the parent amide. Therefore, this method is used for stepping down the series in organic conversions.

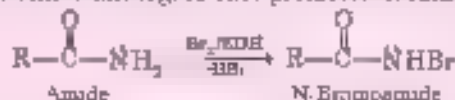


The reaction involves the migration of alkyl group from carbonyl in the precursor to nitrogen with the elimination of CO_2 . Therefore, the reaction provides the product containing one carbon atom less than the starting material.

Mechanism : Hoffmann Bromamide reaction

The reaction is believed to proceed by the following sequence of steps

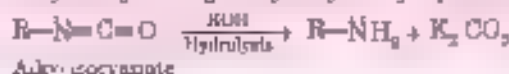
Step 1 The amide undergoes base promoted bromination to form N-bromamide



Step 2 The N-bromamide reacts with OH^- ion to form an anion which rearranges spontaneously with the loss of a Br^- ion to form an isocyanate

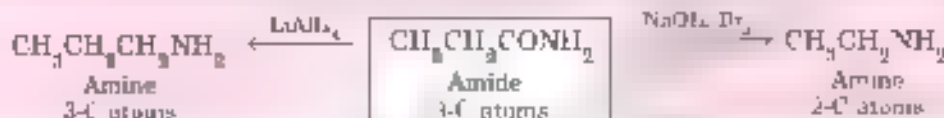


Step 3 The alkyl isocyanate gets hydrolysed by aqueous base to form an amine and carbonate ion.



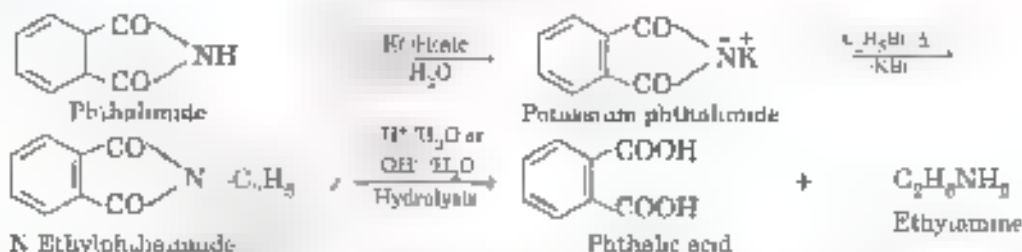
NOTE

It may be noted that primary amines can be obtained from amides either by reduction with LiAlH_4 or by treating with Br_2 and NaOH . The reduction with LiAlH_4 gives amine having same number of C-atoms as the original amide while oxidation with NaOH/Br_2 gives amine having one carbon atom less than the original amide.



6. Gabriel phthalimide synthesis

This method is used for preparing only primary amines. In this method phthalimide is treated with a solution of KOH to give potassium phthalimide which is treated with alkyl halide or benzyl halide to form N-alkyl or aryl phthalimide. The hydrolysis of N-alkyl phthalimide with 20% HCl under pressure or refluxing with NaOH gives primary amine.



Phthalic acid can again be converted into phthalimide and is used again and again. This method is very useful because it gives pure amines.

It may be noted that the hydrolysis of N-alkylphthalimide with aqueous acid or base is generally slow. The more convenient method is by the treatment of alkyl phthalimide with hydrazine NH_2NH_2 .



REMEMBER

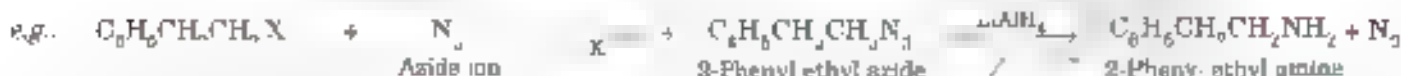
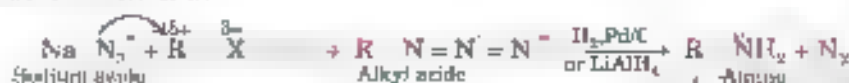
Aryl amides cannot be converted to aryl amines by Gabriel synthesis because they do not undergo nucleophilic substitution with potassium phthalimide. Therefore aromatic primary amines such as aniline, toluidines etc. cannot be prepared by this method.

7. Reduction of azides

Primary amines can be prepared from alkyl halides by first converting the alkyl halide to alkyl azide. Alkyl azides are prepared by nucleophilic substitution of alkyl halides by sodium azide. Then alkyl azides are reduced to alkyl amines with sodium and alcohol or lithium aluminium hydride or by catalytic hydrogenation with H_2 , $\text{Pd}-\text{C}$.

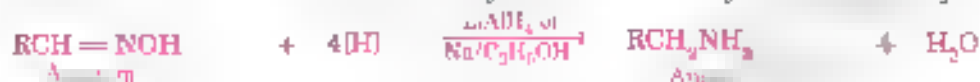


The reaction may also be written as



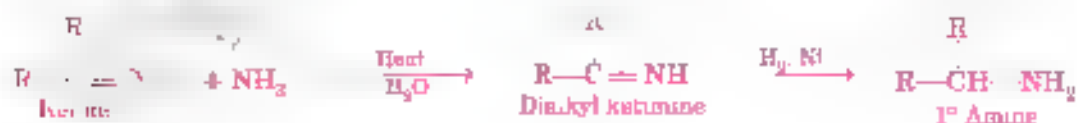
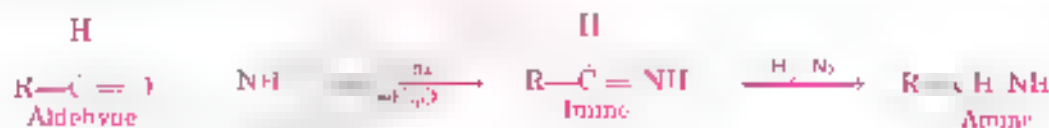
H. By reduction of oximes

Primary amine can be prepared by the reduction of oximes of aldehydes and ketones with either $\text{Na/C}_2\text{H}_5\text{OH}$ or LiAlH_4 . The oximes can be obtained from aldehydes and ketones by reaction with hydroxylamine.



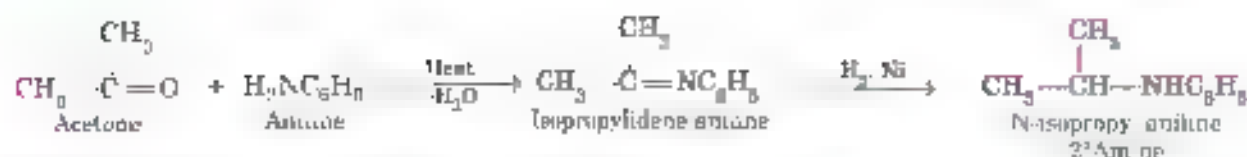
9 Reductive amination of aldehydes and ketones

Primary amines may be prepared by reacting aldehyde or ketone with ammonia to form intermediate imines which can be reduced with H_2, Ni .

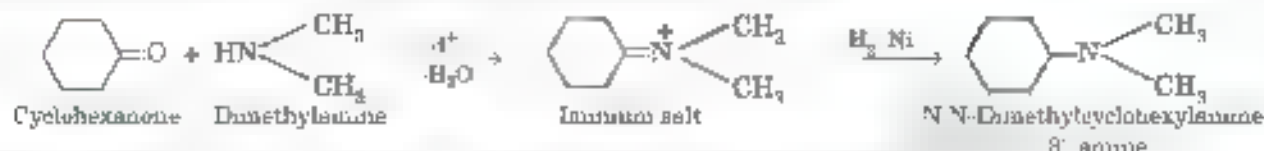


This reaction leading to the conversion of an aldehyde or a ketone to the corresponding amine on treatment with ammonia in the presence of a reducing agent H_2 , NH_3 is called **reductive amination**.

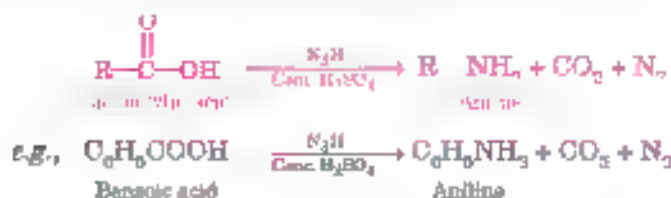
It may be noted that if instead of NH_3 , a primary amine is used in the above reaction, secondary amine is obtained. For example,



Similarly with secondary amines, tertiary amines are formed. For example,



10. Schmidt reaction: Carboxylic acids react with hydrazoic acid (N_3H) in the presence of conc. H_2SO_4 to form primary amines with the evolution of CO_2 and N_2 .



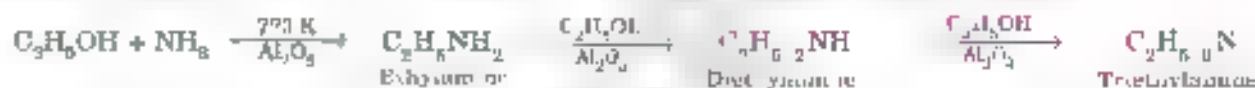
REMEMBER

N_3H is hydrazoic acid and N_3^- is azide ion e.g. NaN_3 sodium azide

Instead of conc. H_2SO_4 and N_3H , a mixture of NaN_3 and conc. H_2SO_4 can also be used.

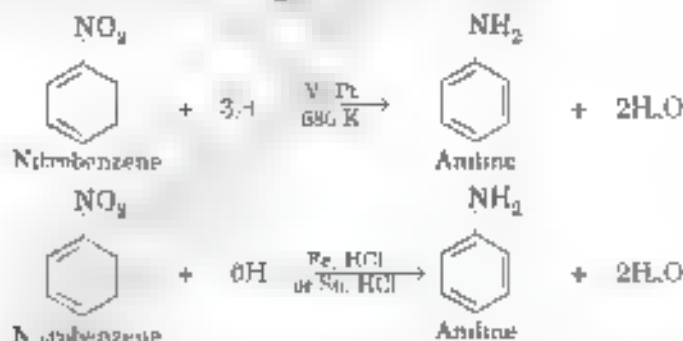
INDUSTRIAL PREPARATION OF AMINES

1. From alcohols: In an industrial scale aliphatic amines are prepared by passing vapours of an alcohol and ammonia over alumina at 723 K. This reaction is called **Sauerbrey and Madhevar method**.



The mixture of three amines is separated by fractional distillation.

2. Aniline: In an industrial scale, aniline is prepared by the reduction of nitrobenzene by catalytic hydrogenation (H_2/Pt or V or Cr_2O_3) or by chemical means using Fe/H^+ or Sn/H^+ .



Aniline is also prepared on a large scale by treating chlorobenzene with ammonia at 473 K and 60 atm pressure using copper oxide as catalyst.



WORKED EXAMPLE 4

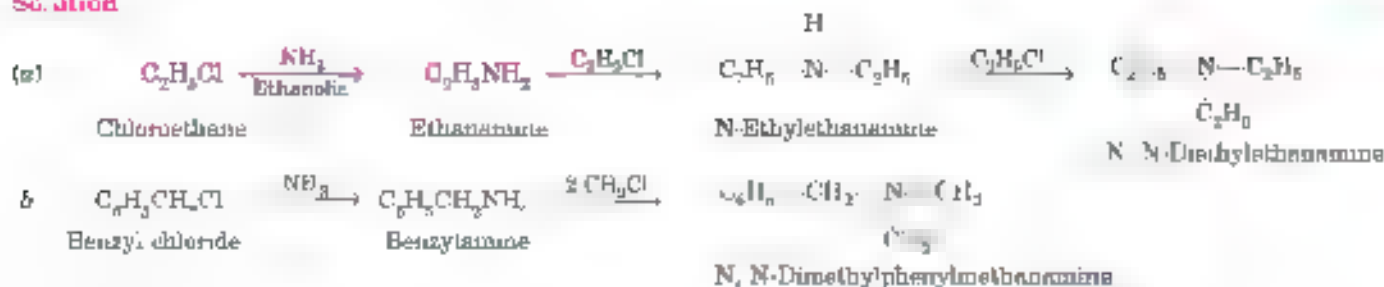
Example 4.

Write chemical equations for the following reactions

(a) Reaction of ethanolic NH_3 with $\text{C}_2\text{H}_5\text{Cl}$

(b) Ammonolysis of benzyl chloride and reaction of aniline so formed with two moles of CH_3Cl

50. **Answer: A**

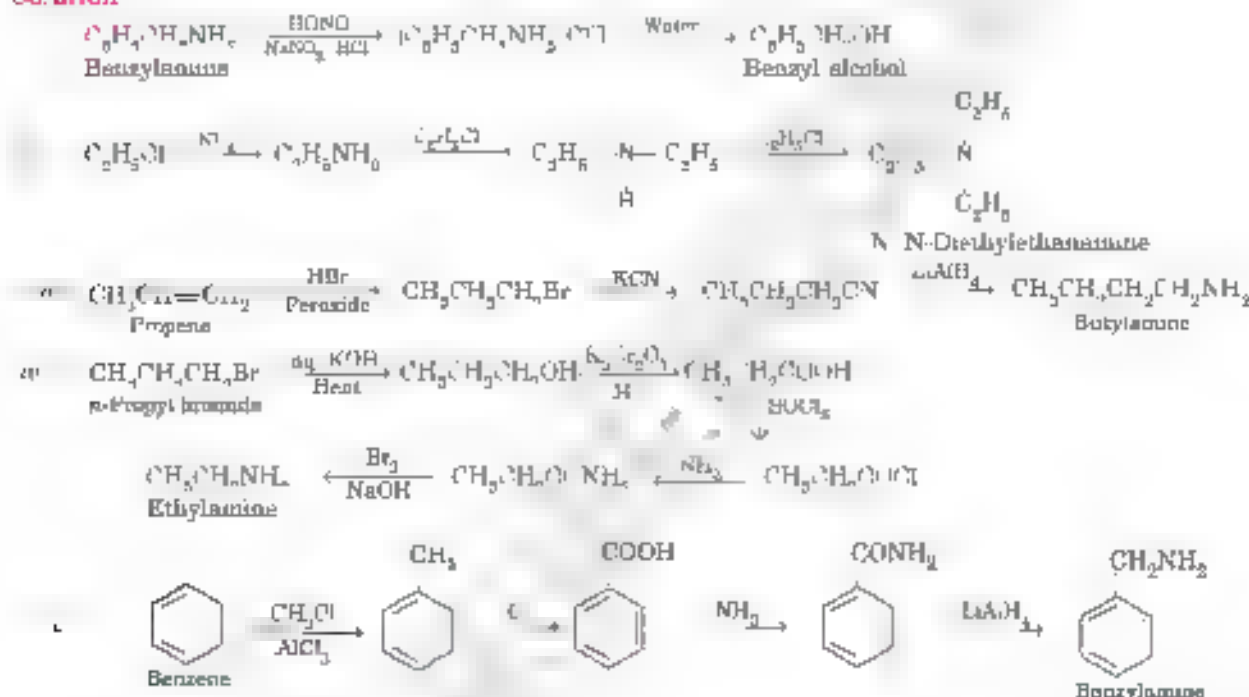


□ **Example 5.**

Write chemical equations for the following conversions:

- (i) $C_6H_5CH_2NH_2$ into $C_6H_5CH_2OH$ (ii) C_2H_5Cl into $(C_2H_5)_3N$
(iii) Propene into butylamine (iv) *n*-propyl bromide into ethylamine
(v) Benzene into benzylamine

See also 1437



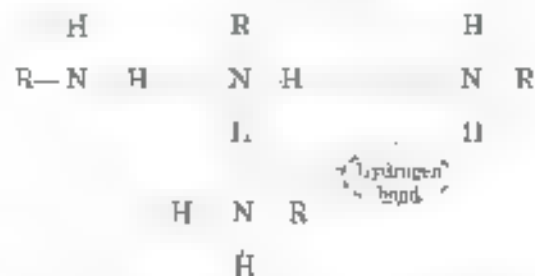
PHYSICAL PROPERTIES OF AMINES

The important physical properties of amines are given below

1 Physical state and smell. Lower members of the aliphatic amines family such as methyl amine, dimethyl amine, ethylamine are gases at ordinary temperatures and have smell like ammonia. The higher members with three or more α atoms are mostly liquids having fishy smell and still higher ones are solids. Most of the amines have unpleasant odour. Aromatic amines, in general are toxic. Most of the amines in pure form are colorless but as they are easily oxidised, they become coloured due to impurities and atmospheric oxidation.

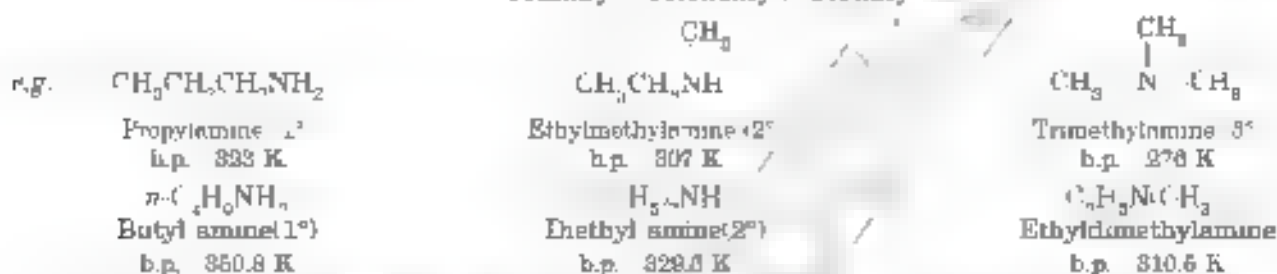
2. Boiling points. Amines have higher boiling points than hydrocarbons of comparable molecular masses. This is due to the reason that amines are polar compounds and with the exception of tertiary amines form associated molecules due to intermolecular hydrogen bonding between nitrogen of one and hydrogen of another molecule as shown alongside.

However amines have lower boiling points than those of alcohols or carboxylic acids. This is due to the reason that electronegativity of nitrogen (3.0) is lower than that of oxygen (3.5) and therefore, O—H bonds present in alcohols and carboxylic acids are more polar than the N—H bond in amines. As a result, the hydrogen bonds in alcohols and carboxylic acids are

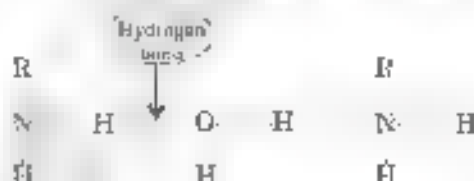


Compound	Molar mass	b.p. (K)	Compound	Molar mass	b.p. (K)
$\text{CH}_4, \text{C}_2\text{H}_6, \text{C}_3\text{H}_8$	44	231	$n\text{-C}_2\text{H}_5\text{Cl}$	78	309
$\text{CH}_3\text{CH}_2\text{NH}_2$	45	290	$n\text{-C}_4\text{H}_9\text{NH}_2$	73	350.8
CH_3CHO	44	293	$n\text{-C}_4\text{H}_9\text{OH}$	74	390.5
$\text{CH}_3\text{CH}_2\text{OH}$	46	351	$n\text{-C}_6\text{H}_5\text{COOH}$	122	474.4
HCOOH	46	374			

Primary > Secondary > Tertiary



3. Solubility. The lower aliphatic amines are soluble in water because they are capable of forming hydrogen bonds with water. However, solubility decreases with increase in molar mass of amines due to increasing size of the hydrophobic alkyl part. Therefore, the higher amines containing six or more carbon atoms are insoluble. Because of their weaker hydrogen bonds, the solubility of amines in water is less than that of alcohols. This is because electronegativity of nitrogen is lower (3.0) than that of oxygen, 3.5 and therefore, amines form weaker hydrogen bonds as compared to alcohols and carboxylic acids. For example, butan-1-amine is less soluble than butan-1-ol. The amines are also soluble in less polar solvents like ether, alcohol or benzene, etc.



CHEMICAL PROPERTIES OF AMINES

Fig. 1 Pyramidal shape of amine
R may be 1

Amines have a lone pair of electrons in nitrogen atom. Due to the presence of lone pair on N atom of the NH_2 group, the amines are generally basic in nature. These are more basic than water and therefore get protonated by water to form alkyl ammonium or aryl ammonium hydroxides which ionize to furnish OH^- ions in solutions.



This reaction is similar to the reaction of ammonia with water



Similarly



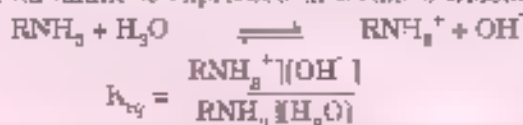
2° Amine



3° Amine

Due to the presence of hydroxide ions, the aqueous solutions of amines are **basic in nature**

The base strength of an amine is expressed in terms of **dissociation constant, K_b** . For the reaction,



Since $[\text{H}_2\text{O}]$ is constant, it is convenient to incorporate it into equilibrium constant as

$$K_{eq}[\text{H}_2\text{O}] = \frac{[\text{RNH}_3^+][\text{OH}^-]}{[\text{RNH}_2]}$$

$$\text{or } K_{eq}[\text{H}_2\text{O}] = K_b = \frac{[\text{RNH}_3^+][\text{OH}^-]}{[\text{RNH}_2]}$$

$$\text{Thus, dissociation constant, } K_b = \frac{[\text{RNH}_3^+][\text{OH}^-]}{[\text{RNH}_2]}$$

Greater the K_b value, the stronger is the base.

The base strength of amines can also be expressed in terms of pK_b values which is defined as

$$pK_b = -\log K_b$$

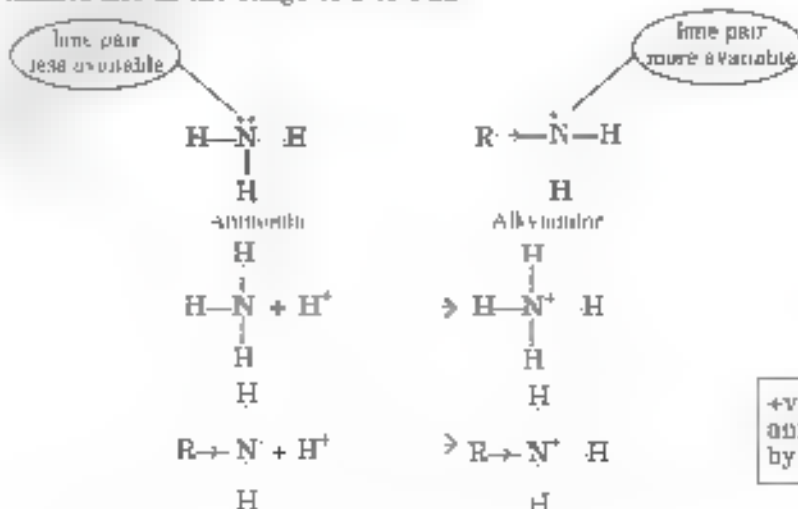
The smaller the value of pK_b , more is the basic strength of amine.

Structure - Basicity Relationship of Amines Comparison of Basic Character of Amines

The basicity of any amine depends upon the ease with which it accepts a proton from the acid to form the ammonium cation. In other words, the basic character of an amine depends upon the stability of the ammonium cation it forms after accepting a proton. *The more stable the ammonium cation is with respect to the cation, more basic is the amine.*

(a) Comparison of aliphatic amines and ammonia

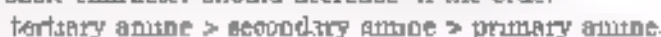
Aliphatic amines are stronger bases than ammonia. This is due to the reason that alkyl groups are electron-releasing +I inductive effect. As a result of electron-releasing effect of an alkyl group, it increases the electron density on the nitrogen atom and therefore, they can donate electron pair of electrons more easily than ammonia. Moreover, the substituted ammonium ion formed from the amine gets stabilised due to dispersal of positive charge by the +I inductive effect of the alkyl groups. **Thus, alkylamines are more basic than ammonia.** For example, K_b value of NH_3 (1.8×10^{-5}) and ethylamine ($K_b = 5.6 \times 10^{-4}$) shows that ethylamine is stronger base. The pK_b value of NH_3 is 4.75 while pK_b values of amines lies in the range of 3 to 4.22



+ve charge on substituted ammonium ion gets dispersed by +I effect of R group

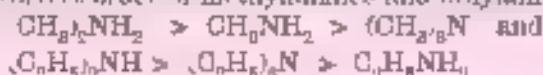
(b) Comparison of basic strength of primary, secondary and tertiary amines.

Due to the presence of lone pair of electrons in amines, they are basic in character. The alkyl group is electron releasing group + I inductive effect and it will increase the electron density on nitrogen and therefore, its basic character should increase. Moreover, the basic character of aliphatic amines should increase with increase in number of alkyl groups. As a result, the basic character should decrease in the order







This trend is followed in the gaseous phase

However in aqueous solutions, it has been observed that tertiary amines are **unexpectedly less basic than the others**. For example, the correct order of methylamines and ethylamines is



The K_b values of some amines are given in Table 1.

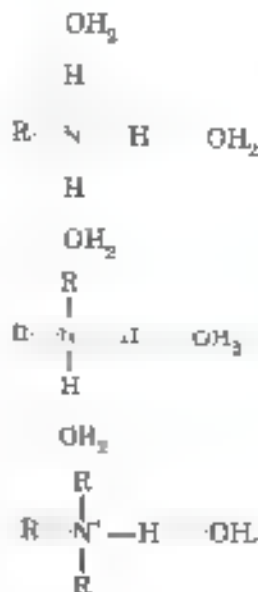
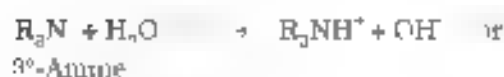
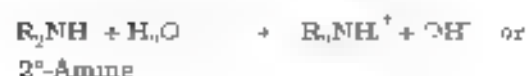
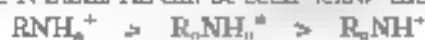
Table 1. Basicity constants of some amines.

Amine		K_b	μK_b	Amine		K_b	μK_b
Ammonia	NH_3	1.8×10^{-5}	4.75	Aniline		4.2×10^{-10}	9.38
Methylamine	CH_3NH_2	4.6×10^{-4}	3.33				
Dimethylamine	$(\text{CH}_3)_2\text{NH}$	6.4×10^{-4}	3.27	N-Methyl aniline		5.1×10^{-10}	9.30
Trimethylamine	$\text{CH}_3)_3\text{N}$	6.0×10^{-5}	4.22				
Ethylamine	$\text{CH}_3\text{CH}_2\text{NH}_2$	6.1×10^{-4}	3.29	N,N-Dimethylethylamine		1.46×10^{-9}	8.93
Diethylamine	$\text{CH}_3\text{CH}_2)_2\text{NH}$	10.0×10^{-4}	3.00				
Triethylamine	$(\text{CH}_3\text{CH}_2)_3\text{N}$	6.8×10^{-4}	3.25	Benzylamine		2.0×10^{-9}	4.70

This may be explained on the basis of following factors

1. Steric factor. The size of alkyl group is more than that of hydrogen and therefore, it hinders the attack of acid on the amine and therefore, basic strength decreases. Now crowding of alkyl group increases from primary to tertiary amines. As a result, their basic strength decreases. This is called **steric hindrance**. According to this effect, tertiary alkyl amines should be least basic.

2. Solvation of ions. When amines are dissolved in water, they undergo hydration through hydrogen bonding. The substituted ammonium cations form hydrogen bonds with water molecules and release energy called *hydration energy* and therefore, get stabilised. Now, greater the extent of hydrogen bonding in ammonium cations, more will be its stabilization and consequently greater will be the tendency of amine to change into cation and *greater will be the strength of the corresponding amine*. The stability of ammonium cation due to hydrogen bonding depends upon the number of H-atoms present on the N-atom. As can be seen below, the hydration of protonated amine due to hydrogen bonding decreases as



Maximum hydration



Minimum hydration

Thus, tertiary ammonium ion is less hydrated than secondary ammonium ion, which is less hydrated than primary ammonium ion. Thus, tertiary amines have less tendency to form ammonium ion and consequently, they are least basic.

Thus, the order of basicity of aliphatic amines should be



This order is opposite to the order based on inductive effect.

As a consequence of combined effects of inductive effect and solvation, the secondary amines are the strongest bases among amines and basic strength varies as



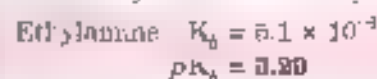
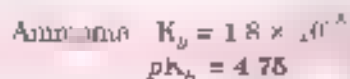
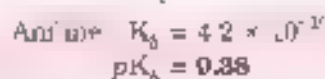
Further, when the alkyl group is small, such as $-\text{CH}_3$ group, there is no steric hindrance to hydrogen bonding. But, in case the alkyl group is bigger than $-\text{CH}_3$ group, there will be steric hindrance to hydrogen bonding. Thus, the change of nature of the alkyl group e.g. from $-\text{CH}_3$ to $-\text{C}_6\text{H}_5$ results in change of the order of basic strength.

It may be noted that in the gas phase, where the solvent effect is missing, the basic trend is as expected, i.e.

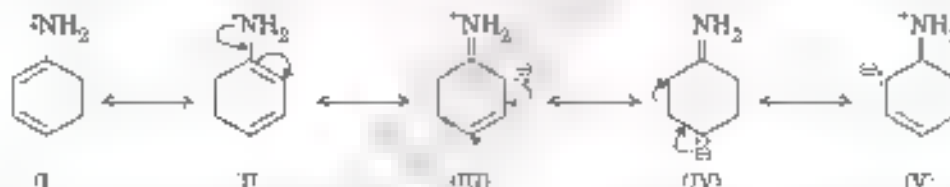


(c) Comparison of basic strength of aromatic amines or arylamines and aliphatic amines.

Aromatic amines or arylamines are less basic than aliphatic amines and ammonia. For example, ethylamine is basic in nature due to the presence of lone pair on N-atom. But aniline is less basic than ammonia as well as ethylamine as shown by K_b values.



In aniline or other aryl amines, the $-\text{NH}_2$ group is attached directly to the benzene ring. As a result, the unshared electron pair on nitrogen atom is present in conjugation with the benzene ring and becomes less available for protonation because of resonance. Aniline may be regarded as resonance hybrid of the following resonating structures.



It is clear from the above resonating structures that three of these structures (III, IV and V) acquire some positive charge on nitrogen. As a result, the pair of electrons become less available for protonation. Hence, aniline is less basic than ethylamine in which there is no such resonance.

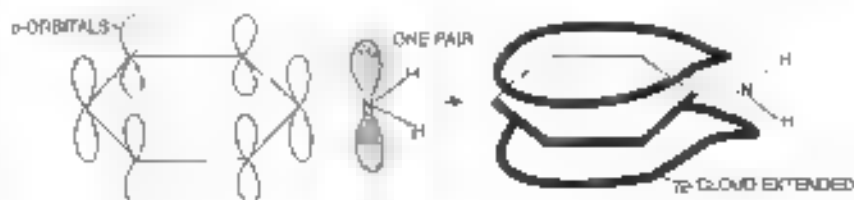
This can also be understood by comparing the relative stability of aniline and anilinium ion obtained by accepting a proton. Anilinium ion can have only two resonating structures.



We know, greater the number of resonating structures, greater is the stability. Now, we observed that whereas aniline has five resonating structures, but anilinium ion has only two resonating structures. Therefore, aniline is more stable than anilinium ion. In other words, aniline has lesser tendency to combine with a proton to form anilinium ion and therefore, aniline is less basic.

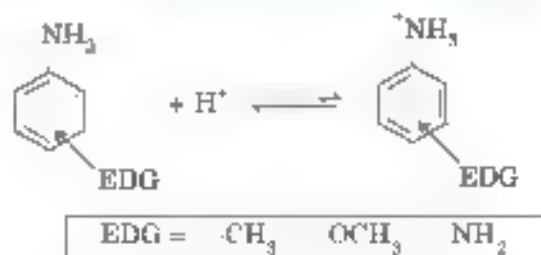
The basic character of aniline can also be understood in terms of **orbital theory**. According to this concept, the orbitals containing the lone pair of electrons on the nitrogen atom interact with π -bonding of the benzene ring system. The delocalised π -cloud gets extended as shown in adjacent structure.

As a result, the lone pair of electrons is not readily available for protonation and therefore, aniline is less basic than ethylamine (alkyl amines).

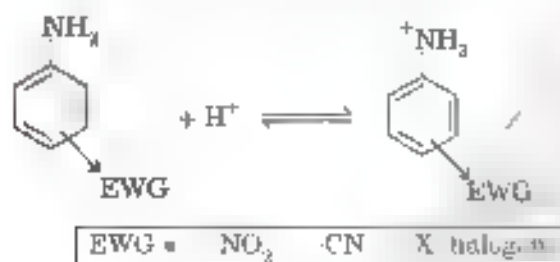


Effect of Substituents on the Basic Character of Aromatic Amines

1. Electron donating or releasing groups like OCH_3 , CH_3 increase the basic strength while electron withdrawing groups like X halogens, NO_2 , CN , SO_3 , COOH etc decrease the basic strength.

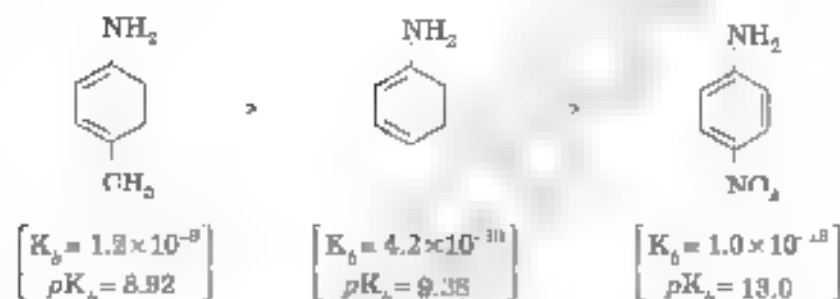


EDG \rightarrow released electrons
stabilized the cation and
increases basic strength



EWG \rightarrow withdraws electrons
destabilized the cation and
decreases basic strength

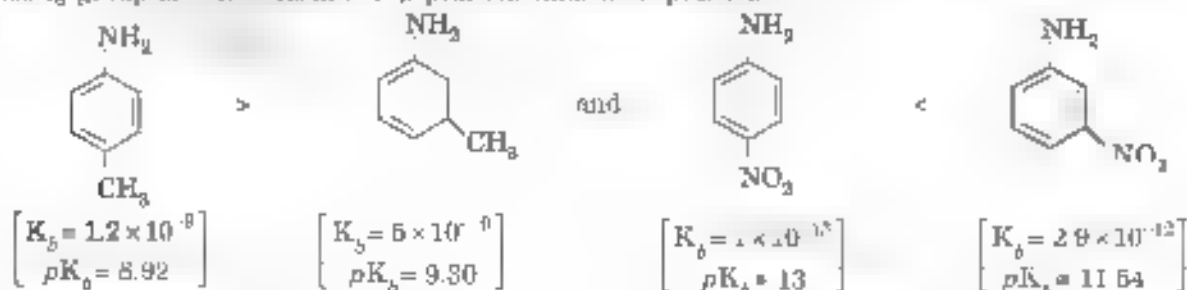
For example,



The basicity constants pK_b of some aromatic amines are given below

Activating group		Deactivating group	
Amine	pK_b	Amine	pK_b
$p\text{-C}_6\text{H}_4\text{CH}_3/\text{NH}_2$	8.93	$p\text{-C}_6\text{H}_4(\text{Cl})/\text{NH}_2$	10.08
$p\text{-C}_6\text{H}_4\text{OCH}_3/\text{NH}_2$	8.60	$p\text{-C}_6\text{H}_4\text{Br}/\text{NH}_2$	10.14
$p\text{-C}_6\text{H}_4\text{NH}_2/\text{NH}_2$	8.5	$p\text{-C}_6\text{H}_4\text{N}/\text{NH}_2$	12.28
Aniline	9.88	$p\text{-C}_6\text{H}_4\text{NO}_2/\text{NH}_2$	13.00

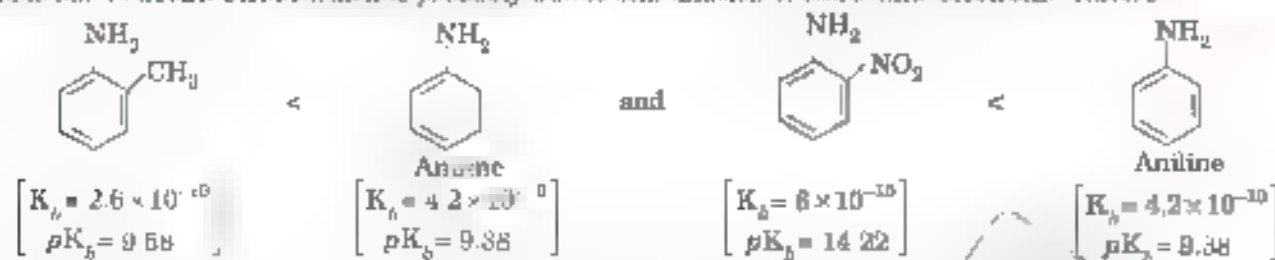
2. The base weakening effect of electron withdrawing group and base strengthening effect of electron releasing group is more marked at p -position than at m -position.



Electron releasing group CH_3 makes
 p -isomer **more stronger basic** than m -isomer

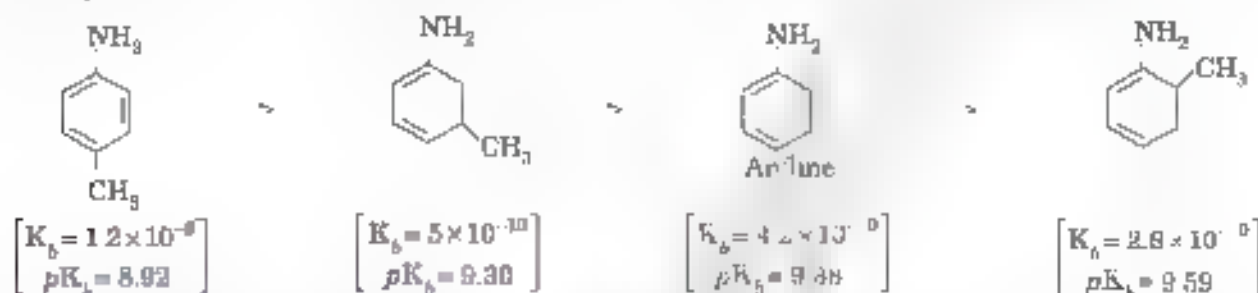
Electron withdrawing group NO_2
makes p -isomer **more weaker base** than m -isomer

1) Every *o*-substituted aniline (electron releasing or electron withdrawing) is less basic than aniline. This is due to **ortho effect** which is probably due to combination of steric and electronic factors.



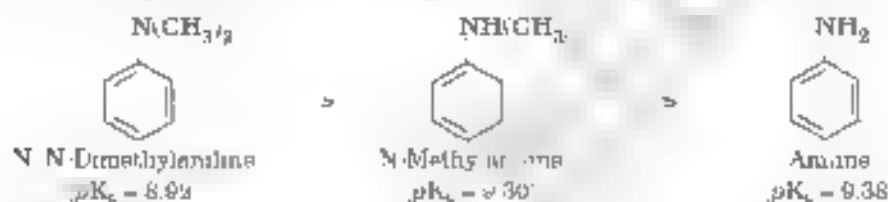
It may be noted that the base weakening effect of electron withdrawing group is **very large** when present at *o*-position than from the *m*- or *p*-position (note aniline and *o*-nitro aniline).

Similarly

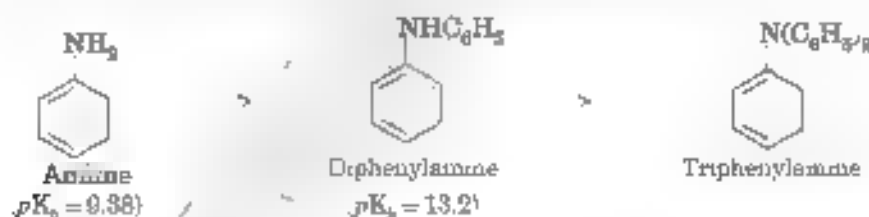


Effect of substituents on the nitrogen atom: *N*-substituted anilines

When hydrogen atoms of the amino group of arylamines are replaced by electron donating alkyl groups, the basic character of the resulting arylamine increases. For example, *N*-methylaniline is a stronger base than aniline and *N,N*-dimethylaniline is even stronger than *N*-methylaniline. Thus,



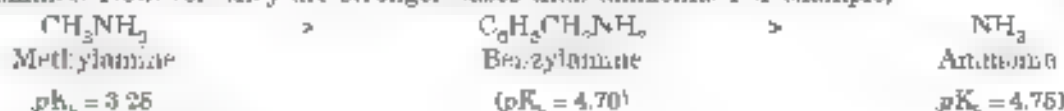
On the other hand, when the hydrogen atoms of amino group are replaced by electron withdrawing groups such as phenyl group, the basic character of the resulting arylamine decreases. For example,



(d) **Comparison of basic character of aralkylamines.** As already learnt, the lone pair of electrons in N-atom of aniline is delocalised over the benzene ring. However, in case of aralkylamines, the lone pair of electrons on the N-atom is not conjugated with the benzene ring and therefore it is not delocalised. Hence, the lone pair of electrons on the N-atom in aralkylamines is more readily available for protonation than that on the N-atom of aniline. Thus, the aralkylamines are more basic than arylamines. For example, benzylamine is a stronger base than aniline.

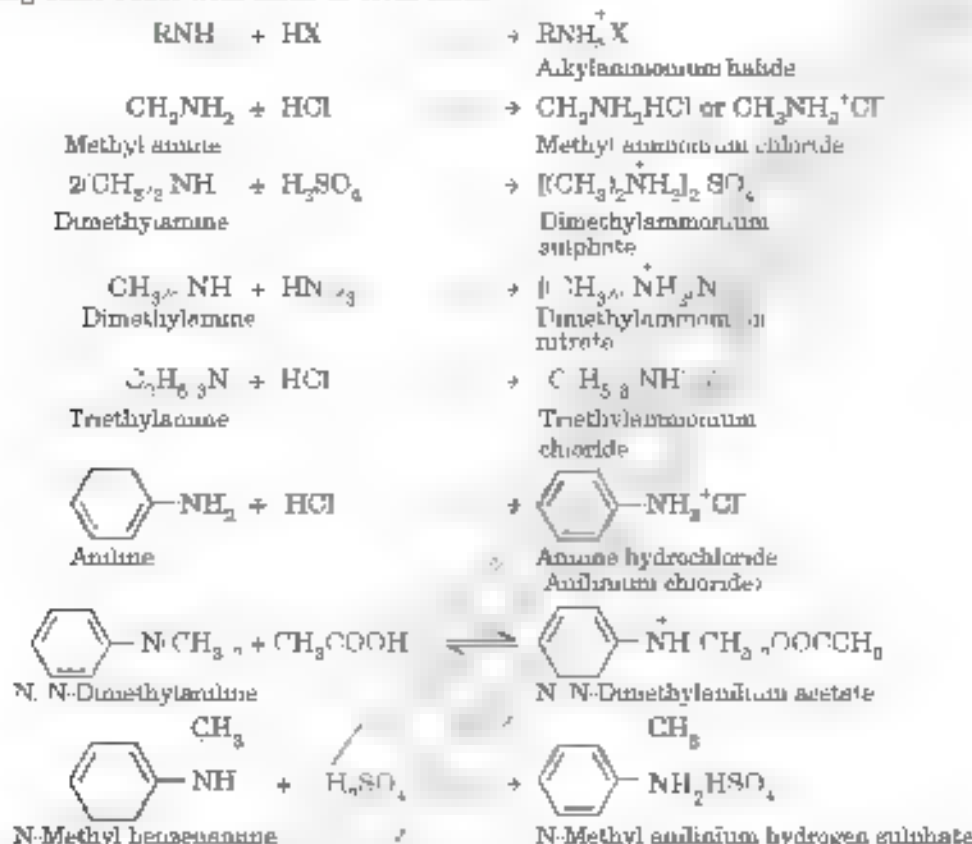


Further *aralkylamines* are *less basic than alkylamines*. This is because aryl group has electron-withdrawing inductive effect (-I effect) while alkyl group in alkyl amines is electron donating group (+I effect). As a result the lone pair of electrons on the N-atom of aralkylamines is less easily available for protonation than that on the N-atom of alkylamines. However they are stronger bases than ammonia. For example,



2. Reaction with acids

Amines being basic react with acids to form salts.

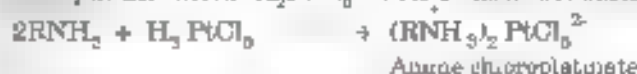


The salts of amines are ionic compounds and are soluble in water. On treatment with aqueous hydroxide, amines are regenerated.



These amine salts are non-volatile solids and generally decompose before their melting points are reached. These are soluble in water but insoluble in non-polar solvents such as benzene, ether, chloroform, etc. This difference in solubility behaviour of amines and their salts is often used to detect amines and separate or purify them from other non-basic impurities.

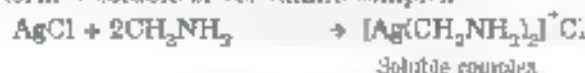
The amines react with chloroplatinic acids H_2PtCl_6 to form insoluble salts called chloroplatinates.



The salts chloroplatinates are used for the determination of equivalent and molecular masses of amines.

3. Reaction of amines with transition metal ions

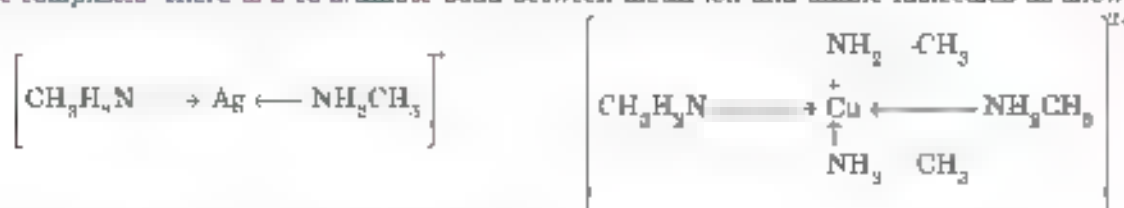
Like ammonia, amines combine with metal ions such as Ag^+ and Cu^{2+} ions to form complex compounds. The lone pair of electrons in NH_3 is used to form a co-ordinate bond of amine with metal ions. For example silver chloride dissolves in methylamine to form a soluble silver amine complex.



Similarly, copper sulphate reacts with methylamine to give deep blue coloured complex.

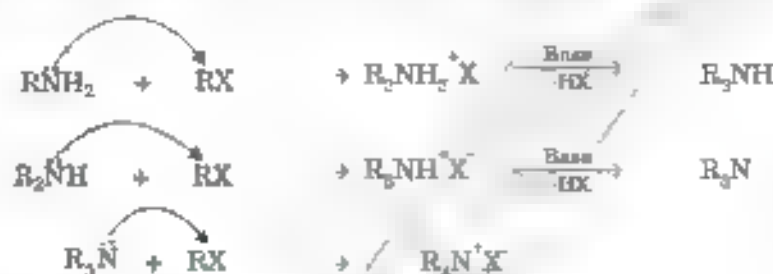


In these complexes there is a co-ordinate bond between metal ion and amine molecules as shown below

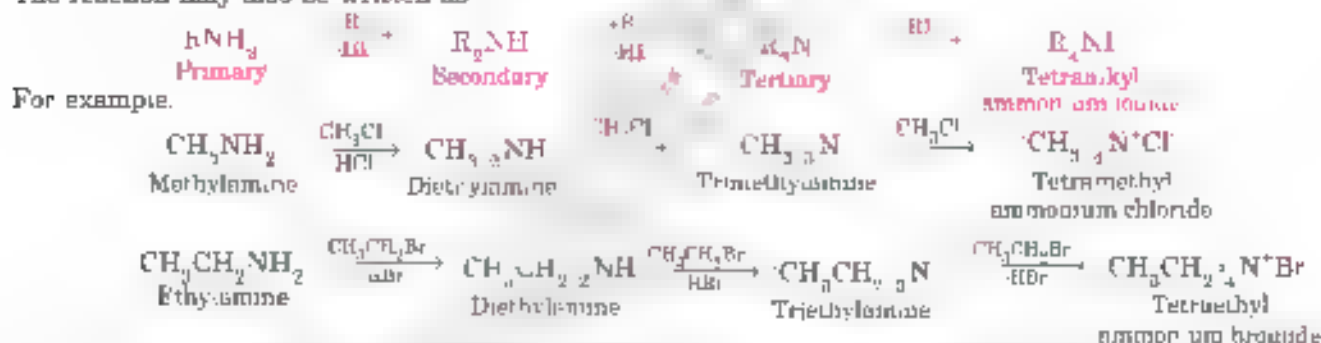


4. Reaction with alkyl halides: Alkylation

Primary and secondary amines react with alkyl halides to form tertiary amines. The primary or secondary amine acts as nucleophile and perform nucleophilic substitution on an alkyl halide. On removal of HX, secondary or a tertiary amine is regenerated respectively. The secondary amine being a more powerful nucleophile again reacts similarly with another alkyl halide forming tertiary amine. At each stage of the reaction, an equivalent amount of a strong acid is formed. This can protonate the amine making lone pair on nitrogen not available for nucleophilic attack and therefore, stop the reaction before completion. Therefore, for the neutralisation of the acid and for liberating the nucleophile, a base such as carbonate is added. Finally, the tertiary amine react with alkyl halides to form quaternary ammonium salts.



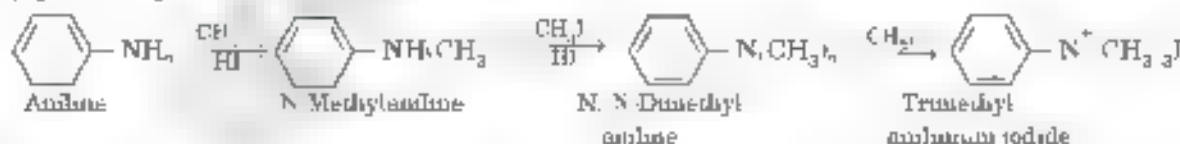
The reaction may also be written as



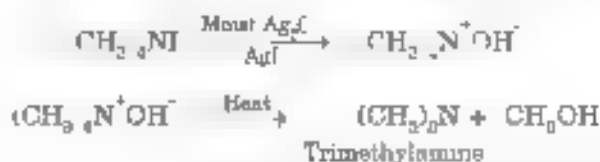
The process of converting an amine 1st, 2nd or 3rd into a quaternary ammonium salt on treatment with excess of alkyl halide is called **exhaustive alkylation**.

If the alkyl halide used is methyl iodide, the process is commonly called **exhaustive methylation**.

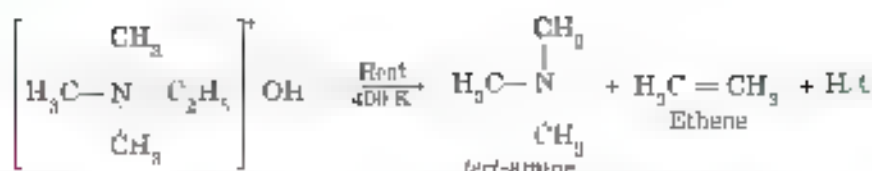
Aromatic amines also undergo similar reactions. For example, when aniline is treated with methyl iodide under pressure, quaternary ammonium salts are formed



The tetramethyl ammonium salt or quaternary ammonium halide on reaction with moist silver oxide forms tetramethyl ammonium hydroxide and silver halide gets precipitated. This on heating (400 K) decomposes to give tertiary amine and alcohol



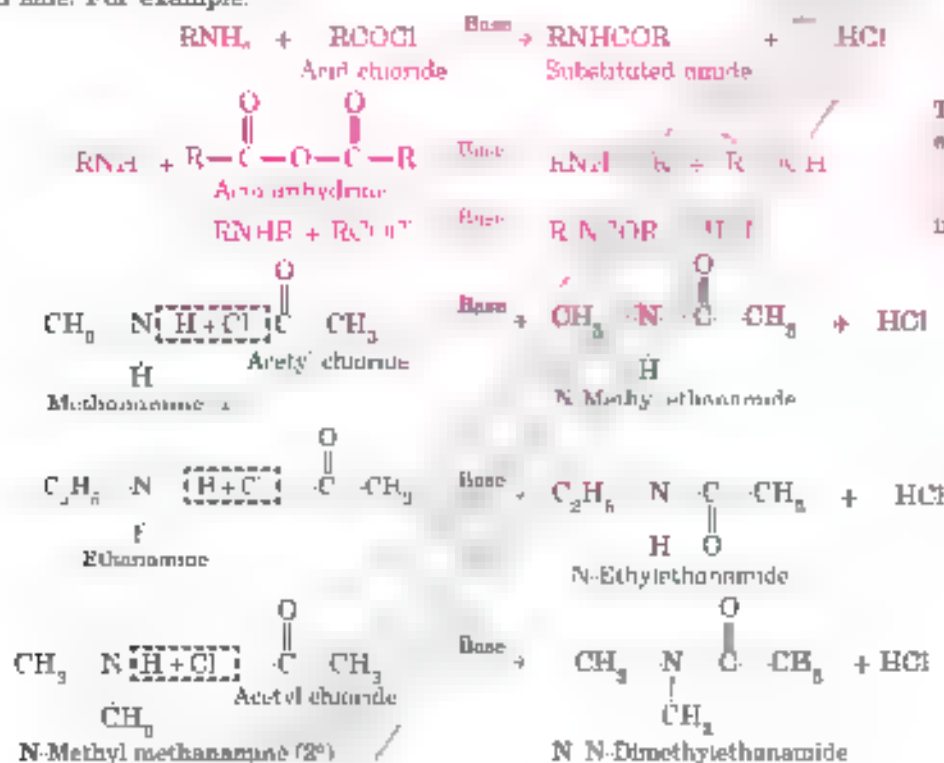
If one of the alkyl groups is other than methyl, the quaternary ammonium hydroxide, gives a tertiary amine and an alkene and water on heating. For example,



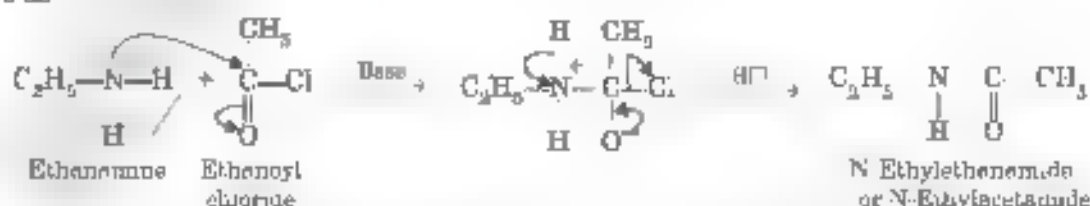
This pyrolysis of quaternary ammonium hydroxide to give alkenes is called **Hoffmann's elimination reaction**. This can be used for the elucidation of the structure of amines.

5. Acylation (reaction with acid chlorides and acid anhydrides)

Aliphatic and aromatic primary and secondary amines which contain replaceable hydrogen atoms react with acid chloride, acid anhydride and esters to form substituted amides. The process of introducing an acyl group $\text{R}-\text{C}(=\text{O})$ into a molecule is called **acylation**. The reaction may be considered as the replacement of hydrogen atom of $-\text{NH}_2$ or $-\text{N}-\text{H}$ group by the acyl group. It is a **nucleophilic substitution reaction**. The reaction is carried out in the presence of a base stronger than amine like pyridine which removes HCl so formation and shifts the equilibrium to the right hand side. For example,



The reaction occurs as

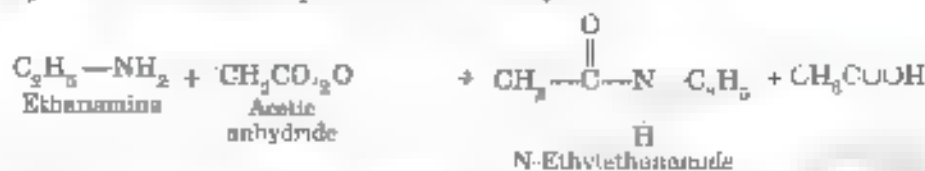


During the reaction, the acid generated can form salt of the amine which will then lose nucleophilic character and therefore, the reaction will not go to completion. Therefore, a base is added to facilitate the reaction. Unlike alkylation, the amide formed does not react further with organic halide because amide is non-basic. The lone pair of electrons on nitrogen is in conjugation with carbonyl group and therefore, it is a poor nucleophile.

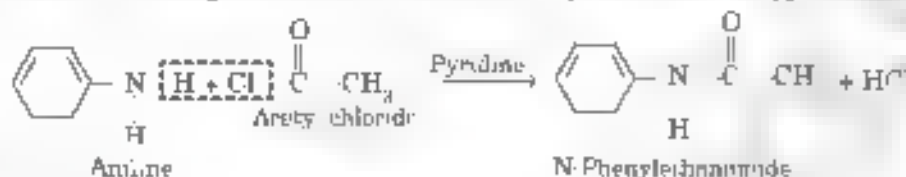


Amongst the acid derivatives the acid chlorides are stronger acylating agents than the anhydrides and esters which react very slowly.

Since tertiary amines do not contain replaceable hydrogen atom, they do not react with acetyl chloride. Therefore, in acylation reaction of an amine in addition to its nucleophilic character, the presence of an H atom on nitrogen is also necessary. Acylation can also take place with acid anhydride.



Aniline or benzenamine reacts in a similar manner. However, acylation of aromatic amines is usually carried out in the presence of a base stronger than the amine such as aqueous NaOH or pyridine. This base removes HCl formed.

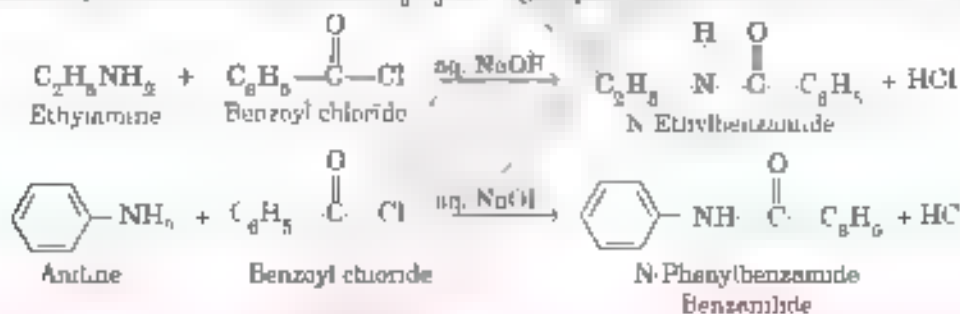


Similarly



8. Benzoylation

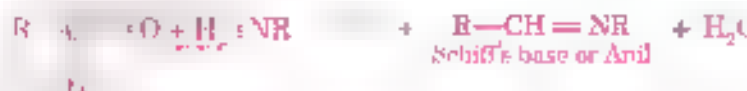
Aliphatic and aromatic amines react with benzoyl chloride in the presence of a base such as pyridine or aqueous NaOH to form benzoyl derivatives in which $\text{C}_6\text{H}_5\text{CO}-$ group is introduced. This reaction is called **benzoylation**.



Benzoylation of compounds containing an active hydrogen such as alcohols, phenols or amines with benzoyl chloride in the presence of dilute aqueous NaOH solution is called **Schotten-Baumann reaction**.

7. Schiff's base formation, reaction with aldehydes and ketones

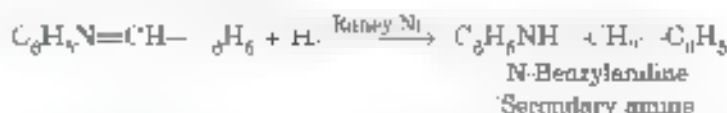
Both aliphatic and aromatic primary amines react with aldehydes and ketones to form amines also called **Schiff's bases** or **anils**.



Benzaldehyde reacts with aniline to give a typical Schiff's base known as **benzal aniline**.

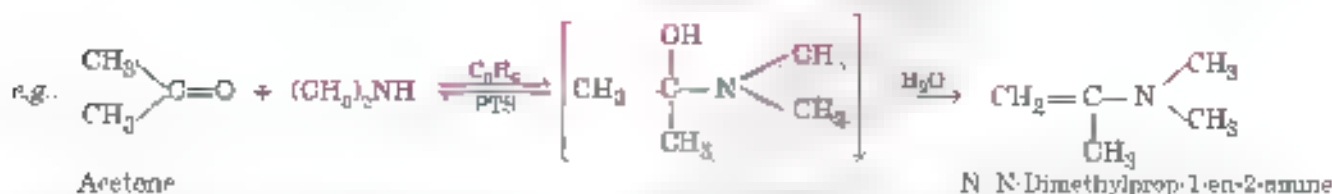


Schiff's base on reductor gives secondary amine.



Therefore, this method can be used to prepare secondary amines.

Aldehydes and ketones which have α -hydrogen react with secondary amines both acyclic e.g. N,N-dimethylamine as well as cyclic e.g. pyrrolidine, piperidine etc. to form carbinolamines. These carbinolamines are unstable and readily lose a molecule of water to form stable α, β -unsaturated amines commonly called **enamines**.
(e.g. e + amine = enamine).



It may be noted that the equilibrium is shifted in the forward direction by removing water as an azeotrope with benzene. Thus, enamine formation is usually carried out by refluxing the benzene solution of an aldehyde or ketone with a secondary amine in the presence of trace amount of an acid such as PTS, *p*-toluene sulfonic acid.

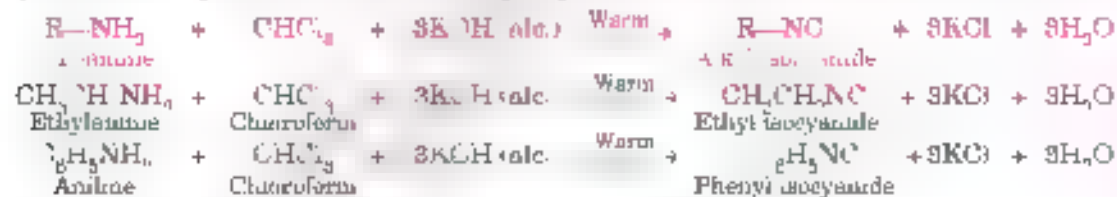
Enamines can also be reduced by catalytic hydrogenation Ni/H_2 or sodium borohydride NaBH_4 to form corresponding amines.



N, N Dimethyl-2-propanamine

H. **Regist on with chloroform.** On treatment reaction of anhydride less

Abstract and aromatic primary amides when warmed with chloroform and an alcoholic solution of KOH form isocyanide or carbodiimide which have very unpleasant or foul smell.



Carbylamine test is an important test to distinguish primary amines from secondary and tertiary amines.

Secondary and tertiary amines do not give this test. Therefore this test can be used to distinguish between primary amines from secondary and tertiary amines.

C. Report it with a copy of the

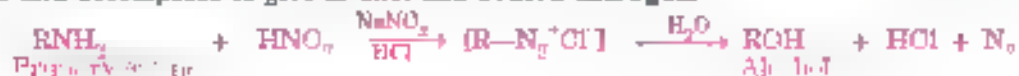
Nitrous acid, HNO_2 , is an unstable acid therefore, it must be freshly prepared *in situ* by treatment of sodium nitrite with cold dilute HCl or H_2SO_4 .

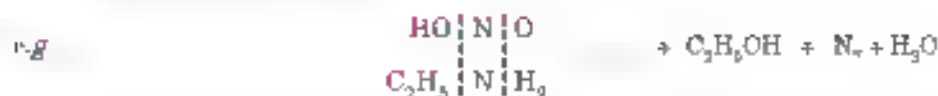


Nitrosonium acid is a source of electrophilic nitrosonium $\text{O}=\text{N}^+$ which reacts with amines

Different classes of amines react differently with nitrous acid. This reaction serves as an important reaction to distinguish between primary, secondary and tertiary amines.

• **Primary amines.** Primary aliphatic amines react rapidly with nitrous acid to form aliphatic diazonium salts, which is unstable and decomposes to give alcohol and evolve nitrogen.

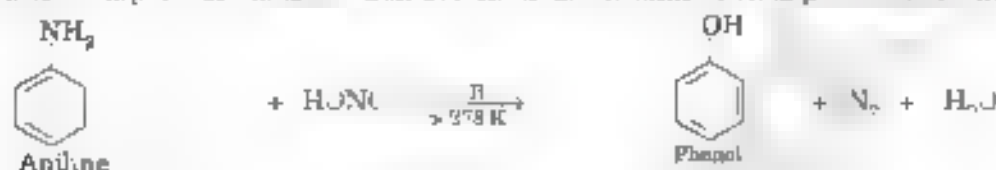




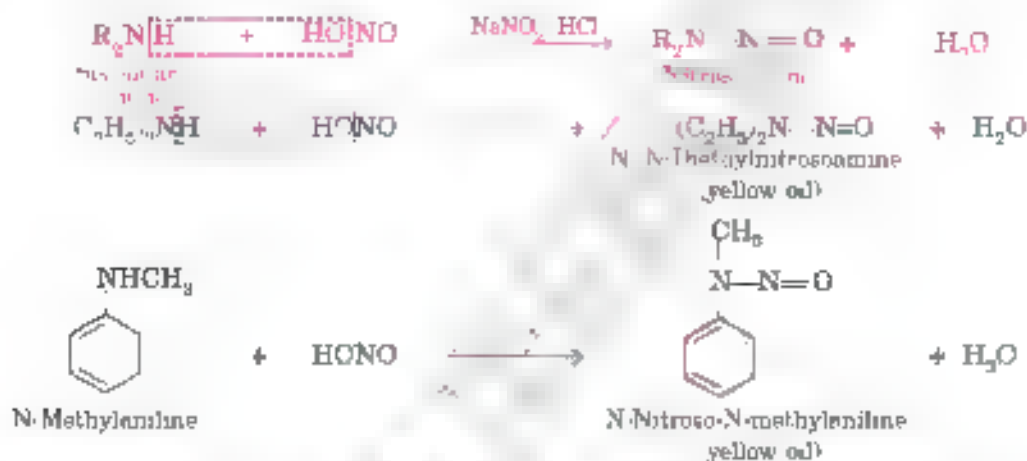
Primary aromatic amines react with nitrous acid in the cold (273–278 K) to form diazonium salts. The process of formation of diazonium salts by the reaction of aromatic amino compound and nitrous acid is called **diazotisation**. For example,



However, if the temperature is more than 278 K, aromatic amines form phenol with the evolution of N_2 gas.

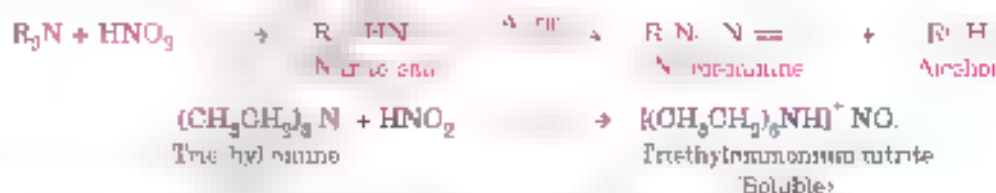


(ii) **Secondary amines.** Secondary aliphatic and aromatic amines react with nitrous acid slowly in the cold to form yellow oily **nitroso amines**.



The yellow oily nitrosoamine gives a **green solution** when warmed with phenol and conc. sulphuric acid. On dilution with water the colour changes to **red**, but it changes to **greenish blue to violet** on the addition of sodium hydroxide. The overall reaction is called **Libermann's nitroso reaction**. This test is used for secondary amines.

(iii) **Tertiary amines.** Tertiary amines dissolve in cold nitrous acid to form salts which decompose on warming to nitrosoamine and alcohol.



Aromatic tertiary amines react with nitrous acid to give coloured substituted nitroso compound. These undergo electrophilic substitution of nitrososulphonation ($\text{N}=\text{O}^+$) at the para position of the phenyl ring.



Are You Curious...



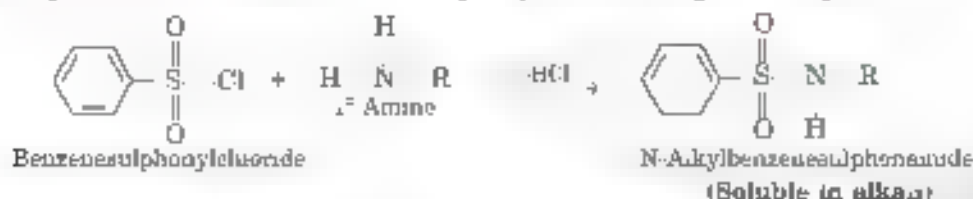
☐ **Cigarette smoking is injurious to health. Do you know why?**

- ◆ In addition to nicotine cigarette smoke contains N-methylnitrosamine which is a powerful carcinogen and very harmful.

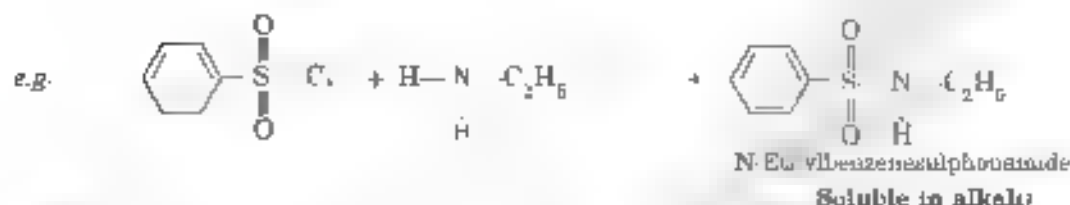
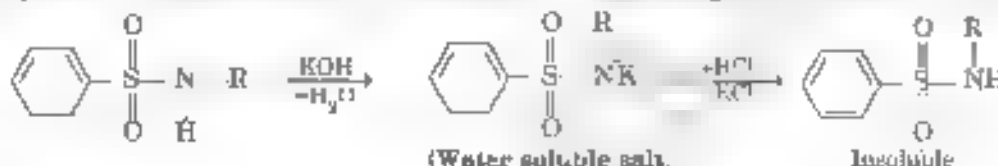
10. Reaction with aryl sulphonyl chloride

Benzene sulphonyl chloride ($\text{C}_6\text{H}_5\text{SO}_2\text{Cl}$) which is also known as **Hinsberg's reagent** reacts with primary and secondary amines to form sulphonamides.

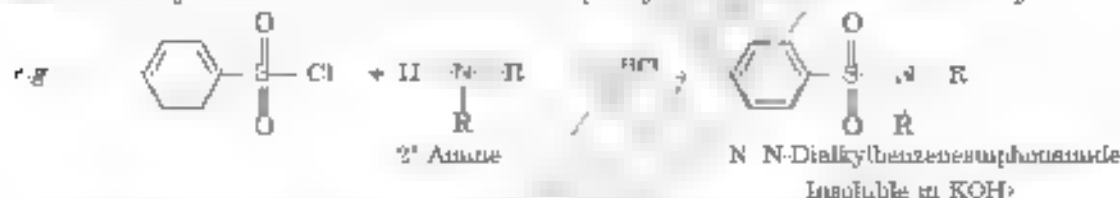
Primary amines react with benzene sulphonyl chloride to give **N-alkyl benzene sulphonamide**



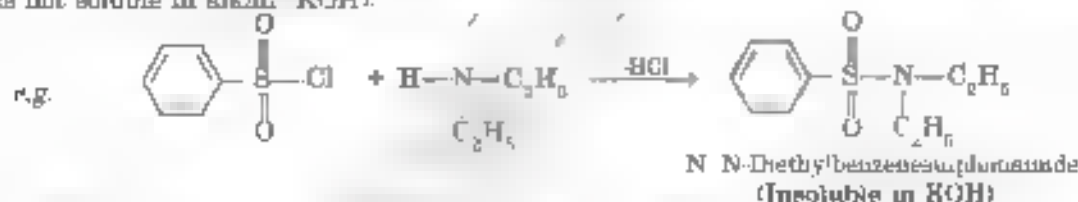
The hydrogen attached to nitrogen in sulphonamide is strongly activated to the presence of strongly electron withdrawing sulphonyl group. Therefore, it is soluble in alkali. In acidification it gives an insoluble material.



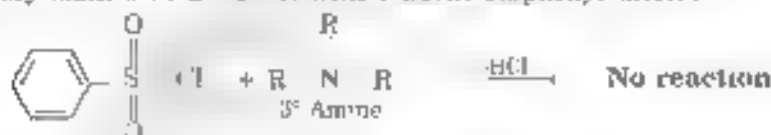
Secondary amines react with benzene sulphonyl chloride to form **N,N-dialkyl benzene sulphonamide**.



Since the sulphonamide does not contain any hydrogen atom attached to nitrogen atom, so it is not acidic. Hence it is not soluble in alkali (KOH).



Tertiary amines do not react with benzene sulphonyl chloride.



Since different amines react differently with benzene sulphonyl chloride this reaction can be used for the **distinction between 1°, 2° and 3° amines** and also for the separation of their mixtures.

However, these days benzene sulphonyl chloride has been replaced by *p*-toluenesulphonyl chloride.

11. Reaction with Grignard reagent

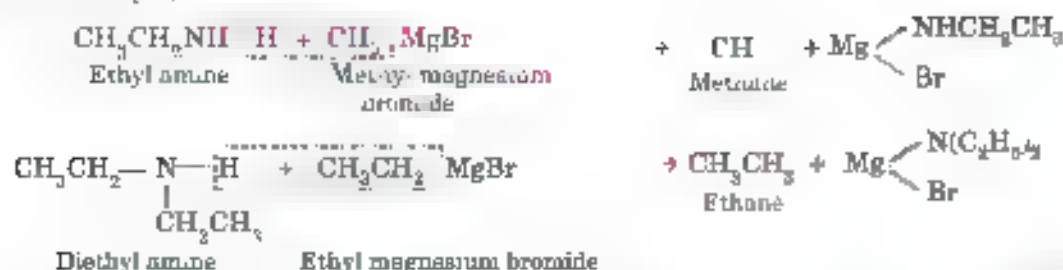
Primary and secondary amines react with Grignard reagents to form **alkanes**



NOTE

It may be noted that alkane is obtained from the alkyl part of Grignard reagent.

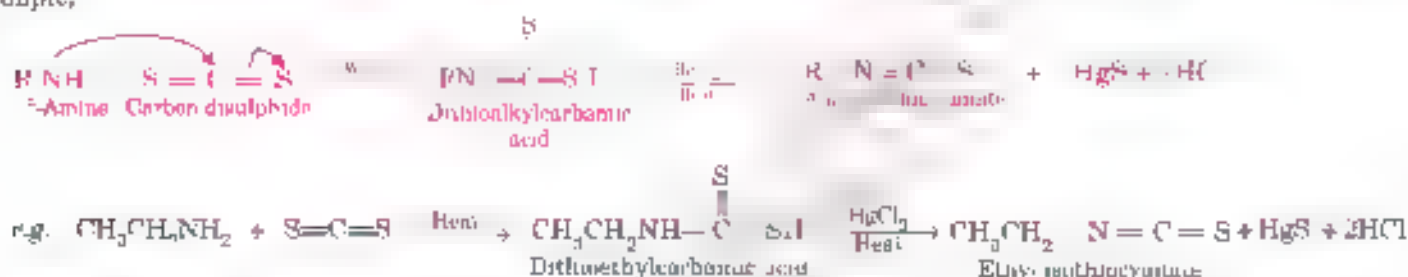
For example,



Tertiary aliphatic amines do not react with Grignard reagent, because they do not have hydrogen atom attached to the nitrogen atom.

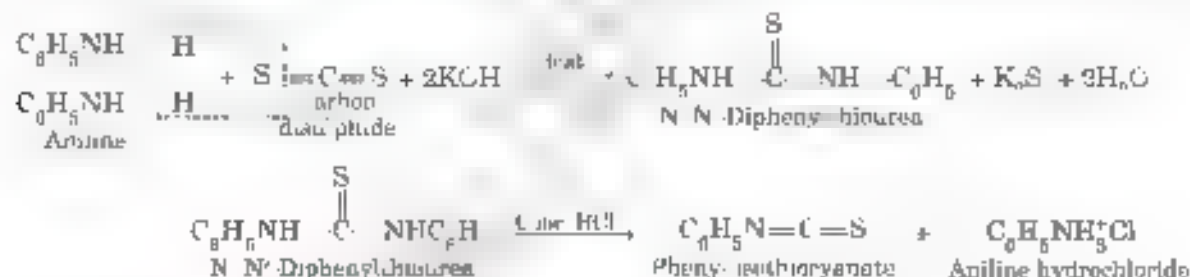
12. Reaction with carbon disulphide

Primary amines react with carbon disulphide to form dithioalkyl carbamic acids which decompose on heating with mercuric chloride (HgCl_2) to give alkyl isothiocyanates. These have character similar like mustard gas. For example,



This reaction is called **Hoffmann mustard oil reaction** and is used as a test for primary amines.

However aromatic amines react in slightly different manner. For example, when aniline is heated with ethanolic CS_2 and acid KOH , it forms N,N-diphenylthiourea which on treatment with conc. HCl gives phenyl isothiocyanate.



N,N-Diphenylthiourea or thiocarbonyl diurea is used as an accelerator during vulcanization of rubber.

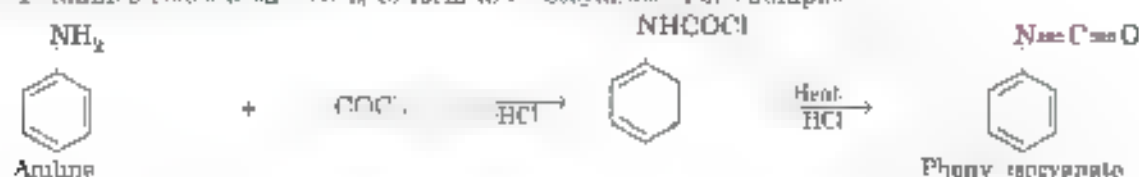
13. Reaction with carbonyl chloride (phosgene)

Primary and secondary aliphatic amines react with carbonyl chloride to form substituted ureas.



Tertiary aliphatic amines form salts.

Aromatic 1^o amines react with COCl_2 to form aryl isocyanate. For example,



14. Oxidation

Oxidation of amines give different products depending upon the nature of amine and oxidising agent. Amines undergo oxidation by powerful oxidising agents such as Caro's acid, H_2SO_5 , potassium permanganate (KMnO_4), hydrogen peroxide (H_2O_2) etc. The products of oxidation depend upon the nature of amine and oxidising agent. For example,

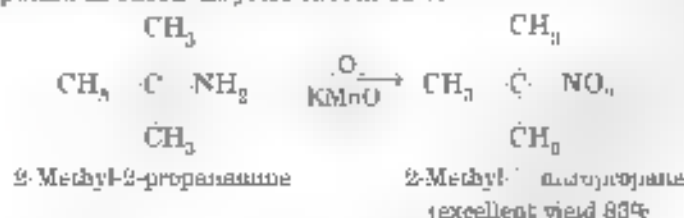
(a) Oxidation of primary amines

Primary aliphatic amines on oxidation with potassium permanganate give nitro compounds through a sequence of reactions as shown below

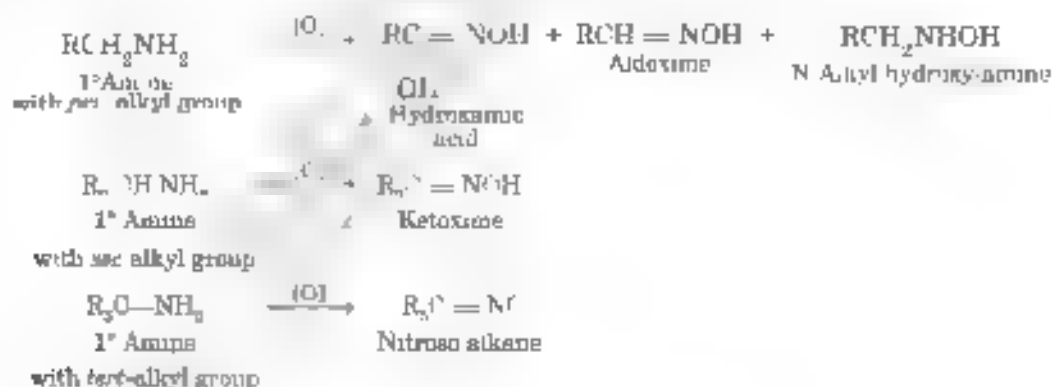


Depending upon the nature of the oxidising agent, various products such as hydroxylamine, nitroso or nitro compounds can be isolated.

Primary amines in which NH_2 group is attached to the tertiary carbon atom can be oxidised with KMnO_4 to the corresponding nitro compound in excellent yield (about 83%).

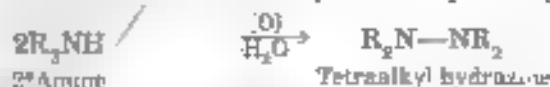


Primary amines react with Caro's acid, H_2SO_5 or H_2O_8 in the following ways



(b) Oxidation of secondary amines

Secondary aliphatic amines on oxidation with potassium permanganate give tetra alkyl hydrazines



Secondary amines with Caro's acid give corresponding N-hydroxy amine



(c) Oxidation of tertiary amines

Tertiary amines are not oxidised by KMnO_4 but are oxidised by Caro's acid, ozone or H_2O_8 to corresponding N-oxides.

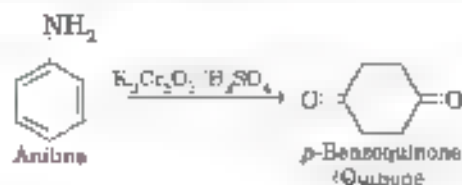


(d) Oxidation of aromatic amines

Aromatic amines, because of high electron density on the benzene ring, are readily oxidised on exposure to air or oxidising agents forming a complex coloured product

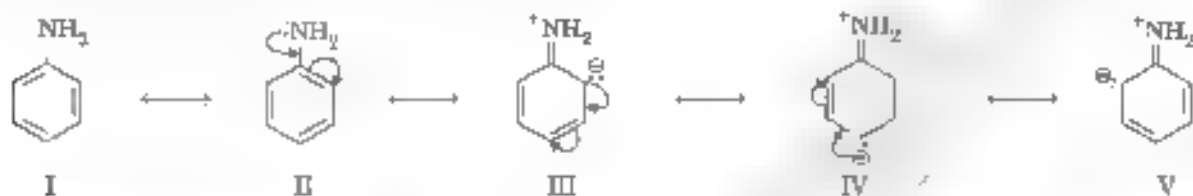


However, controlled oxidation of aniline with $\text{K}_2\text{Cr}_2\text{O}_7$ and H_2SO_4 , gives *p*-benzoquinone



15. Ring substitution in aromatic amines

Aromatic amines give the aromatic substitution reactions as given by benzene. *Aniline is more reactive than benzene.* The presence of amino group activates the aromatic ring and directs the attacking group preferably to *ortho* and *para* positions. This is clear from the following resonating structures in which electron density is more at *ortho* and *para* positions (structures III to IV).



Therefore, substitution mainly occurs at *ortho* and *para* positions. Due to strong activating effect of NH_2 , aromatic amines undergo electrophilic substitution reactions readily. Therefore, it is difficult to stop the reaction to monosubstitution stage. However, in order to stop the reaction to monosubstitution stage the activating effect of the amino group has to be reduced. This can be done by *acetylation* with acetic anhydride in the presence of pyridine. Acetyl group is electron withdrawing group and therefore the electron pair of N-atom is withdrawn towards the carbonyl group as shown by the following resonating structures.

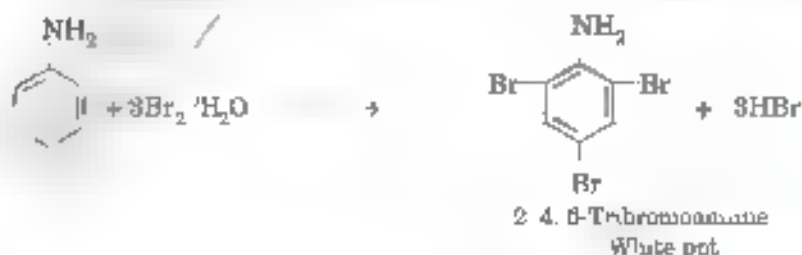


Therefore the lone pair of electrons on nitrogen is less available and the activating power of NH_2 group is decreased. This method is called the **protection** of the amino group by acetylation and can be used to control the rate of electrophilic substitution reaction. This also prevents the formation of *di* and *tri* substituted products.

The acetyl group is then removed by hydrolysis to get back the anine.

Some of these reactions are given below.

(a) **Halogenation.** Aniline reacts with bromine water readily to give a white precipitate of 2, 4, 6-tribromoaniline.

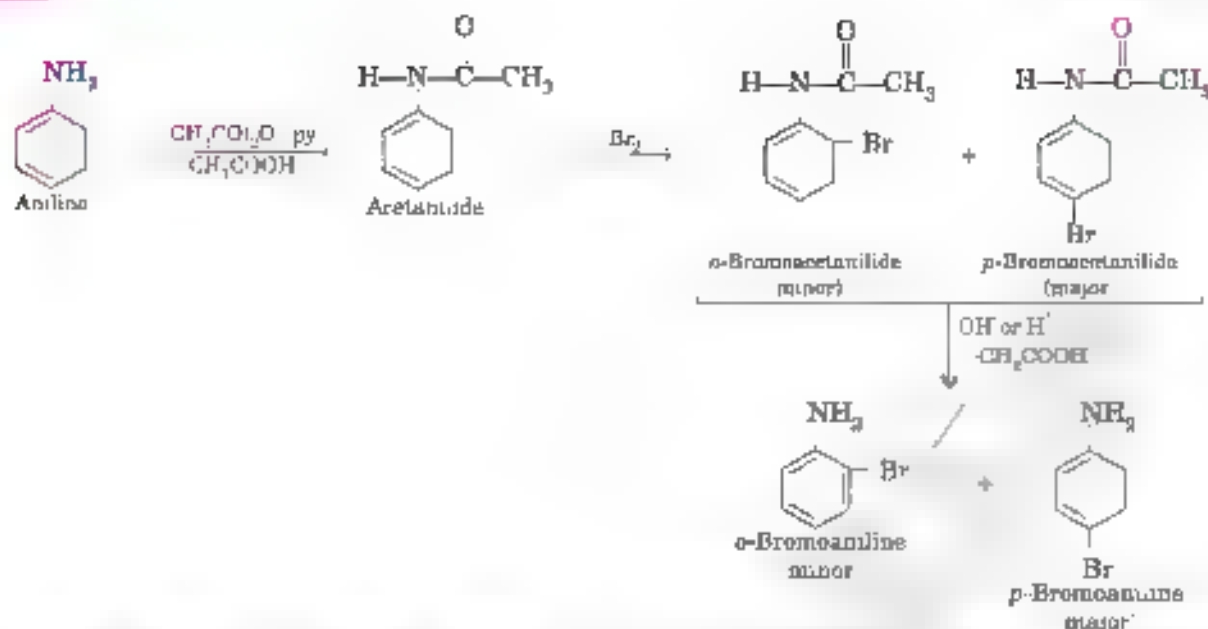


NOTE

This reaction is used as a test for aniline.

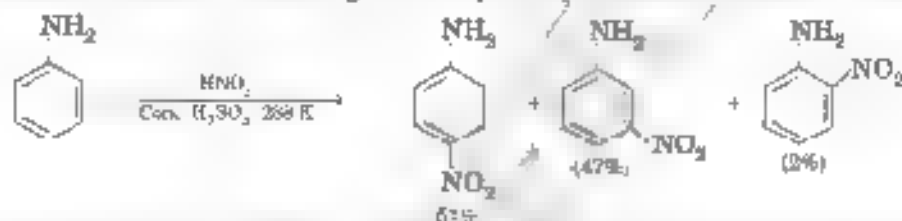
However, if monosubstituted derivative is desired, aniline is first acetylated with acetyl chloride and then halogenation is carried out. After halogenation, the acetyl group is removed by hydrolysis and only monosubstituted halogen derivative is obtained.

It may be noted that NH_2 group directs the attacking group at *o*- and *p*-positions and therefore, both *o*- and *p*-derivatives are obtained.

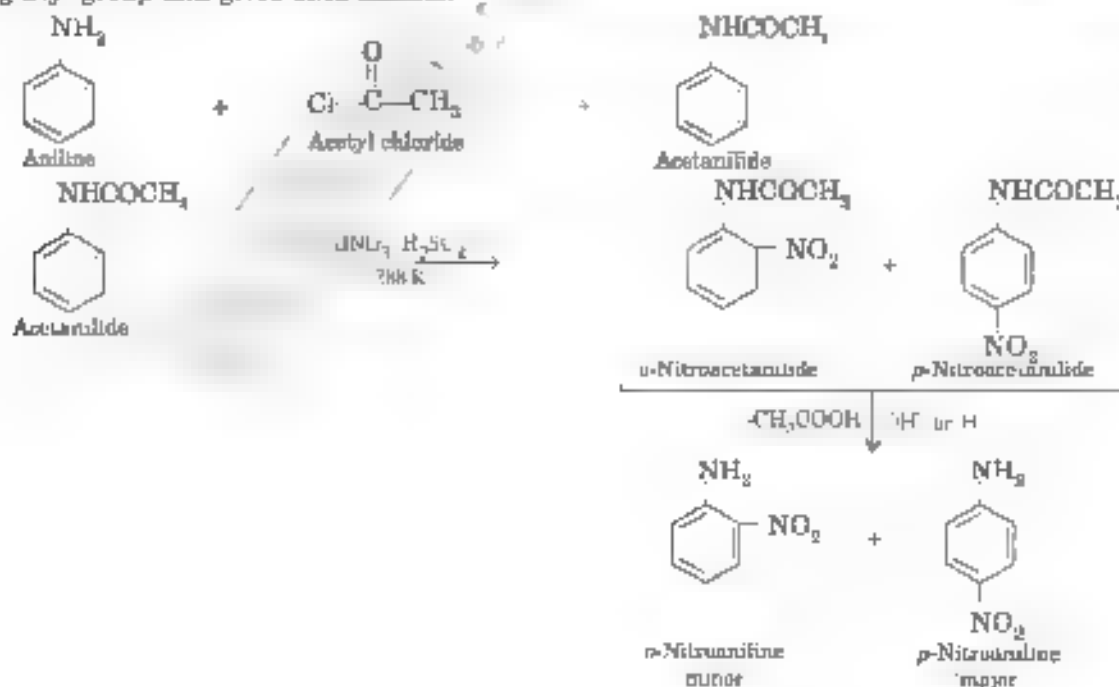


As already explained **acetylation deactivates the ring and controls the reaction to monosubstitution stage only.**

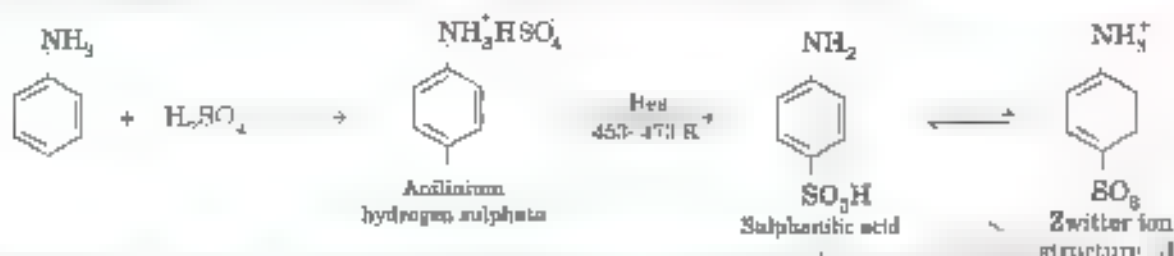
(ii) Nitration: Aromatic amines cannot be nitrated directly because they are readily oxidized. This is because HNO_3 is a strong oxidising agent and results in partial oxidation of the ring to form a black mass. However, under controlled conditions, nitration of aniline gives unexpectedly 47% *m*-nitro aniline in addition to *o*- and *p*-nitroaniline.



The reason for the formation of large amount of *m*-nitroaniline is that under strongly acidic conditions aniline gets protonated to anilinium ion (NH_3^+ group). This is a deactivating group and a meta directing. Therefore, to solve this problem nitration is carried out by protecting the NH_2 group by acetylation. The acetylation deactivates the ring and therefore controls the reaction to monosubstitution stage. The hydrolysis of nitroacetanilides removes the protecting acyl group and gives back amines.



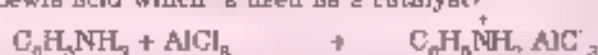
(iii) **Sulphonation.** Sulphonation of aniline is carried out by heating aniline with sulphuric acid. The product formed is anilinium hydrogen sulphate which on heating gives sulphamic acid.



The sulphamic acid exists as a dipolar ion structure II which has amine and acid groups in the same molecule. Such ions are called **Zwitter ions or inner salts**.

NOTE

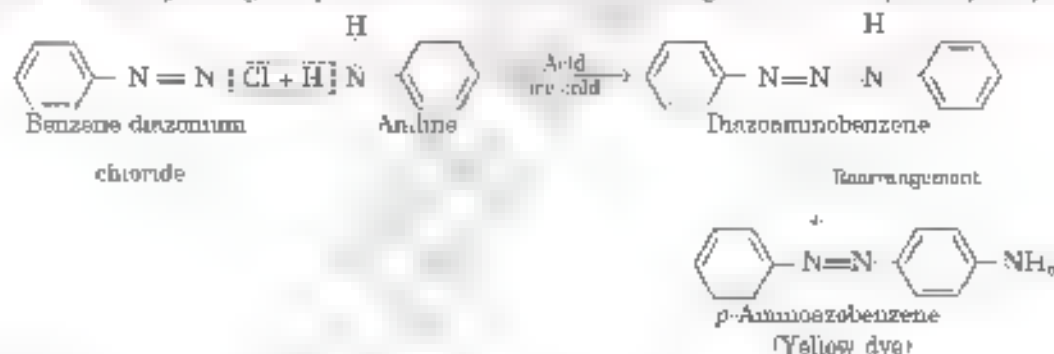
Aniline does not undergo Friedel-Crafts reaction (alkylation and acylation) because of the salt formation with aluminium chloride (Lewis acid which is used as a catalyst):



Nitrogen of aniline acquires positive charge and hence acts as a strong electron withdrawing group. As a result it reduces the electron density of the benzene ring and therefore deactivates it. Hence, aniline does not undergo Friedel-Crafts alkylation or acylation reaction.

18. Coupling with diazonium salts

Aromatic amines react with diazonium salts to form azo compounds in acidic medium called dyes. The reaction is known as **coupling or diazo reaction**. For example, aniline couples with benzene diazonium chloride to form diazo amino benzene which immediately changes to *p*-amino azo benzene on warming with a small quantity of hydrochloric acid.



Tests for amines

1 **Solubility test:** All amines are basic in nature and hence are soluble in dil. HCl. These amines can be regenerated from acidic medium by adding excess of alkali.

2 **Carbylamine test:** Primary amines aliphatic or aromatic can be detected easily by heating the amine with chloroform and alkali, when characteristic foul smell of isocyanides is produced. This test is called **carbylamine test** (Reaction 8).

3 **Liebermann's nitroso test:** Secondary amines aliphatic or aromatic can be detected by **Liebermann's nitroso reaction**, (reaction 9).

4 **Dye test.** Aromatic primary amines give azo dye test (reaction 18).

Uses of amines

The important uses of aliphatic and aromatic amines are given below.

- 1 Aliphatic amines of low molecular mass are used as solvents.
- 2 Amines are also used as intermediates in drug manufacture and as reagents in organic synthesis.
- 3 Aromatic amines are used for the manufacture of polymers, dyes and as intermediates for additives in the rubber industry.
- 4 The quaternary ammonium salts derived from long chain aliphatic tertiary amines are widely used as detergents.
- 5 Aromatic amines are converted into arene diazonium salts which are used for the preparation of variety of aromatic compounds via substitution and coupling reactions.

DISTINCTION BETWEEN PRIMARY, SECONDARY AND TERTIARY AMINES

The following tests can be used to distinguish between primary, secondary and tertiary amines.

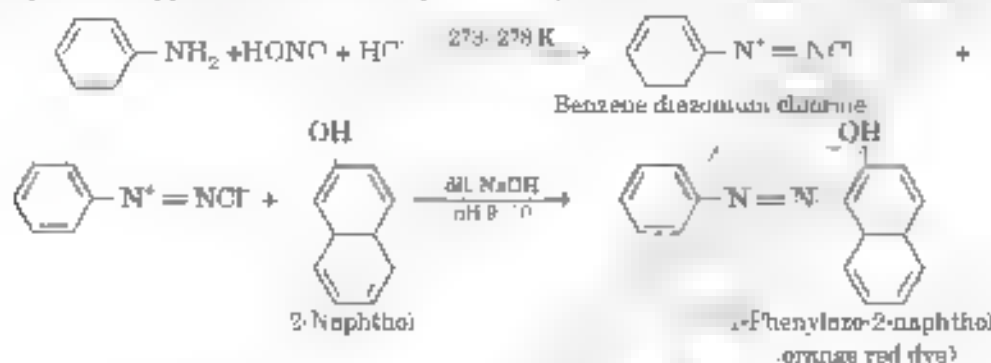
1 **Carbylamine test.** Both aromatic and aliphatic **primary amines** on heating with chloroform in the presence of alcoholic KOH form carbylamines or isocyanides having extremely unpleasant smell. This test is called **carbylamine test** and is used to distinguish primary amines from secondary and tertiary amines (see reaction 8, page 28).

2. Reaction with nitrous acid. The three types of amines react differently with nitrous acid (reaction 9 page 1400-1401).

3. Hinsberg's test for amines. This test is used to distinguish primary, secondary and tertiary amines. In this test the amine is heated with benzene sulphonyl chloride ($\text{C}_6\text{H}_5\text{SO}_2\text{Cl}$) known as **Hinsberg's reagent** in the presence of excess of alkali. Different amines give different observations (reaction 10)

- 1. Primary amines give *clear solution* which on acidification yields an *insoluble material*.
- 2. Secondary amines give an *insoluble substance* which remains unaffected on addition of acid.
- 3. Tertiary amines do not react and remain insoluble in alkali and can be dissolved in acids.

4. Azo dye test. Aromatic primary amines can be distinguished from aliphatic primary amines by **azo dye test**. To perform this test dissolve the primary amine in dil. HCl and cool it to 273-278 K. Treat this solution with ice cold solution of HNO_2 , NaNO_2 + dil. HCl at 273-278 K. Add the resulting solution to cold alkaline solution of 2-naphthol (β -naphthol). Appearance of an orange or red dye confirms the presence of aromatic primary amine.



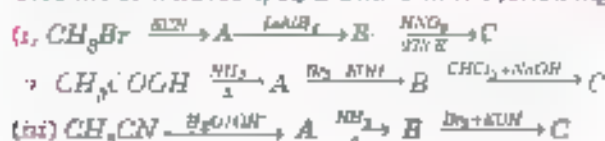
The above tests are summarized below

Characteristic Reaction	Primary	Secondary	Tertiary
1. Reaction with nitrous acid $\text{NaNO}_2 + \text{HCl}$	N is given out with the formation of alcohols $\text{RNH}_2 + \text{HONO} \rightarrow \text{N}_2\uparrow + \text{alcohols}$	Nitrosamines are formed which give a brown color (Nitroso test) $\begin{array}{c} \text{H} \\ \diagdown \\ \text{R}-\text{NH} \\ \diagup \\ \text{R} \end{array} + \text{HONO} \rightarrow \begin{array}{c} \text{R} \\ \diagdown \\ \text{R}-\text{N} \\ \diagup \\ \text{R} \end{array} \cdot \text{N}=\text{O} + \text{H}_2\text{O}$ Nitrosamine	They remain dissolved forming amine nitrite salt which decomposes on warming to nitrosamines and alcohol $\text{R}_3\text{N} + \text{HONO} \rightarrow \text{R}_3\text{NHNO}_2 \xrightarrow{\text{Warm}} \text{R}_2\text{NNO} + \text{ROH}$
2. Carbylamine reaction i.e. with CHCl_3 and alcoholic KOH	Gives foul smelling carbylamine. $\text{RNH}_2 + \text{CHCl}_3 + 3\text{KOH} \rightarrow \text{RNC} + 3\text{KCl} + 3\text{H}_2\text{O}$ Carbylamine	No reaction	No reaction
3. Acylation or reaction with acetyl chloride	Form amides RCONH_2	Form amides $\text{RCON} \begin{array}{l} \text{R} \\ \diagdown \\ \text{R} \end{array}$	No reaction
4. Hinsberg's test	Gives clear solution which on acidification gives insoluble material $\text{RNH}_2 + \text{C}_6\text{H}_5\text{SO}_2\text{Cl} \xrightarrow{\text{H}} \text{C}_6\text{H}_5\text{SO}_2\text{NHR}$ $\xrightarrow[\text{HCl}]{\text{conc.}} \text{C}_6\text{H}_5\text{SO}_2\text{N}^+\text{K}^+ \begin{array}{c} \text{H} \\ \\ \text{R} \end{array}$ (soluble in alkali)	Gives insoluble substance which is not affected by acid $\text{R}_2\text{NH} + \text{C}_6\text{H}_5\text{SO}_2\text{Cl} \xrightarrow{\text{KOH}} \text{C}_6\text{H}_5\text{SO}_2\text{N}(\text{R})_2$ (Insoluble in alkali)	Does not react
5. Azo dye test	Primary aromatic amines give coloured dyes.	No reaction	No reaction

Solved Examples

Example 6.

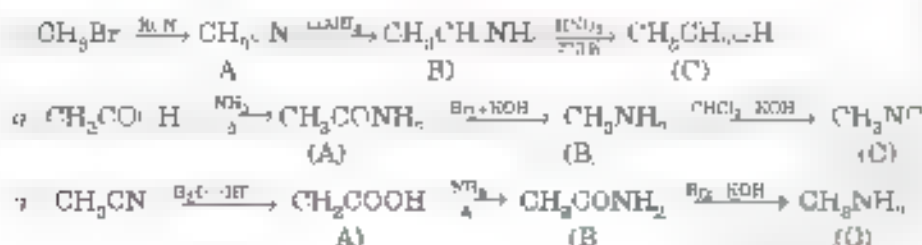
Give the structures of A, B and C in the following reactions:



D.S.B. 2013, 2014

(A.I.S.B. 2014)

Solution:



Example 7

Write structures and IUPAC names of

- the amide which gives propanamine by Hoffmann bromamide reaction
- the alkyl halide used in Gabriel phthalimide synthesis to give ethanamine
- amine obtained by reduction of propanamide
- the amine produced by the Hoffmann degradation of an amide

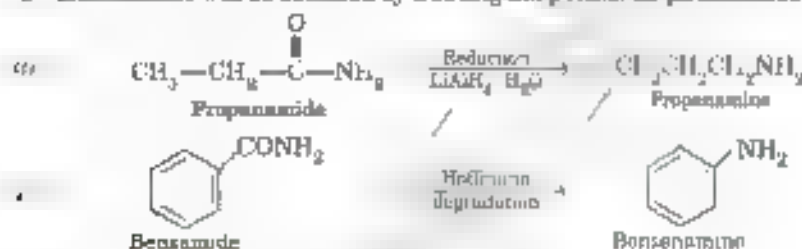
N.C.E.R.T.

N.C.E.R.T.

Solution: Since propanamine contains 3 carbon atoms, the amide molecule must contain four carbon atoms.

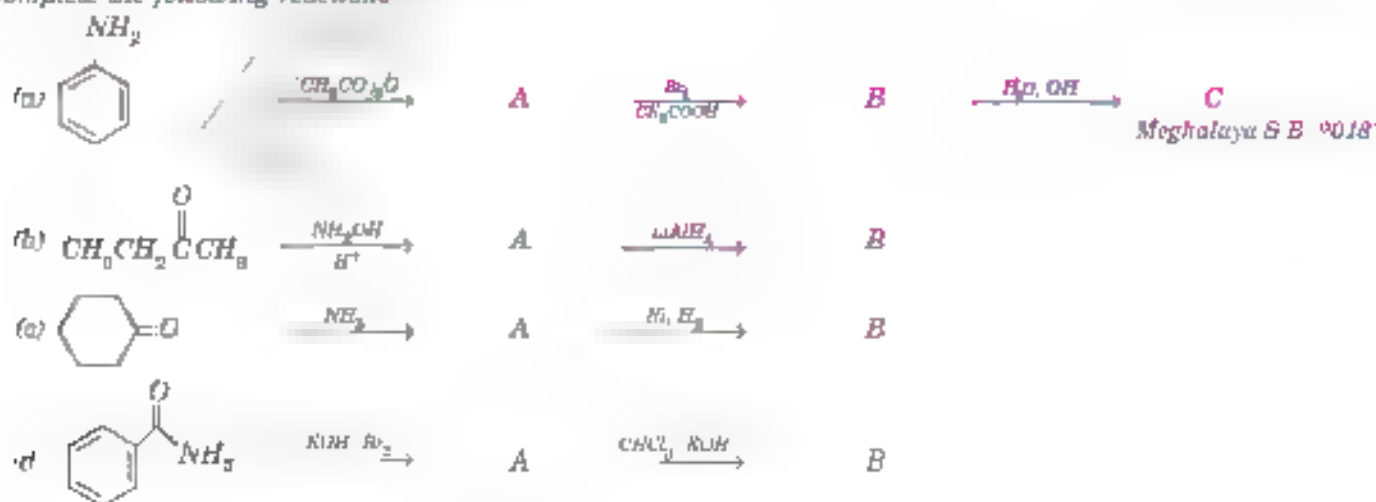


- i. Ethanamine will be obtained by creating the potassium phthalimide salt with bromoethane (ethyl bromide) $\text{H}_3\text{C}-\text{CH}_2\text{Br}$

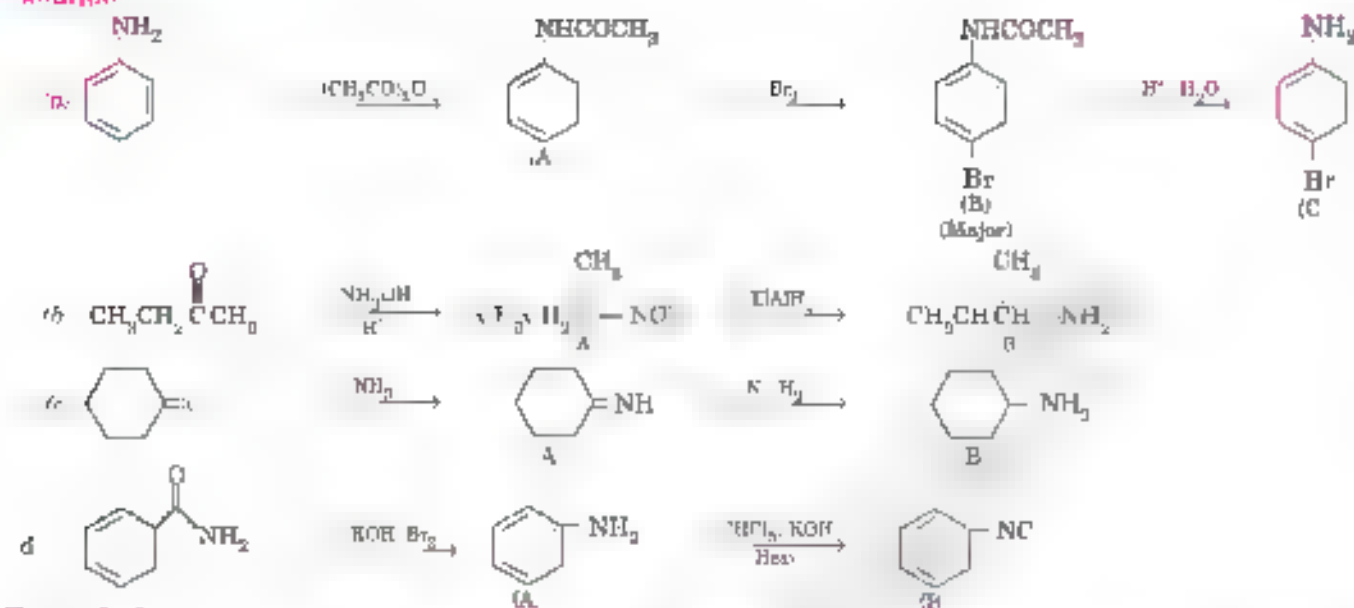


Example 8.

Complete the following reactions



Solution



Example 9.

a. How will you convert an alkyl halide into a primary amine having one more carbon atom than the alkyl halide uses.

b. How can a carboxylic acid be converted into an amine having one more carbon atom than the carboxylic acid used?

Solution a. By heating with KCN followed by treatment with $\text{Na, C}_2\text{H}_5\text{OH}$. For example



b. By forming amide which on reacting with Br_2 and KOH gives amine having one carbon atom less.

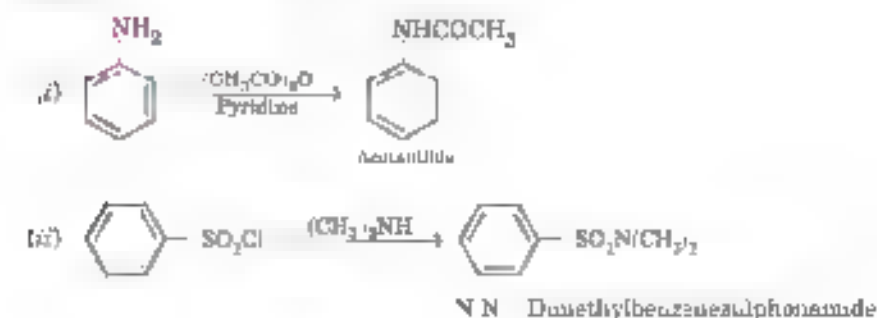


Example 10.

Complete the following reactions:

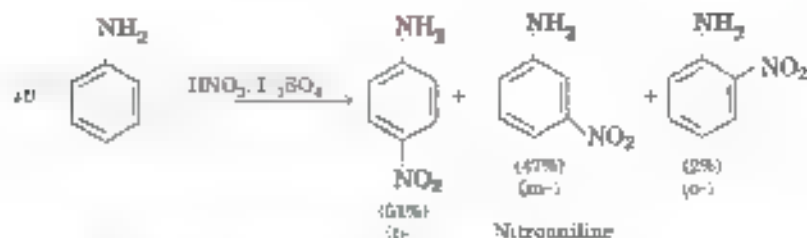


Solution





Ethylamine



Nitroaniline



Phenyl isocyanide

Example 11.

How will you convert the following

1. Nitrobenzene into aniline

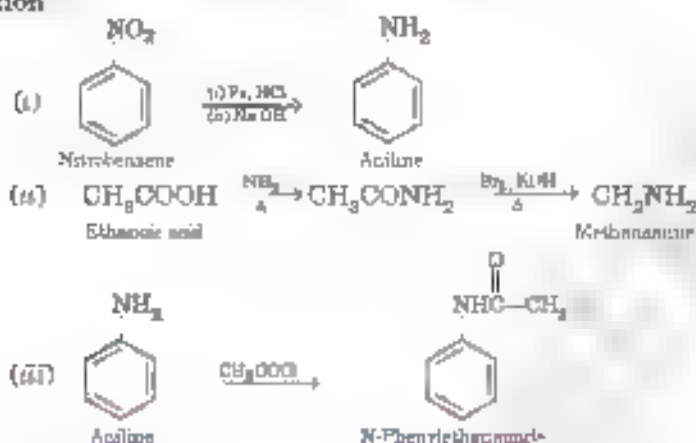
2. Ethanoic acid into methylamine

3. Acetone into N-phenylethanamide

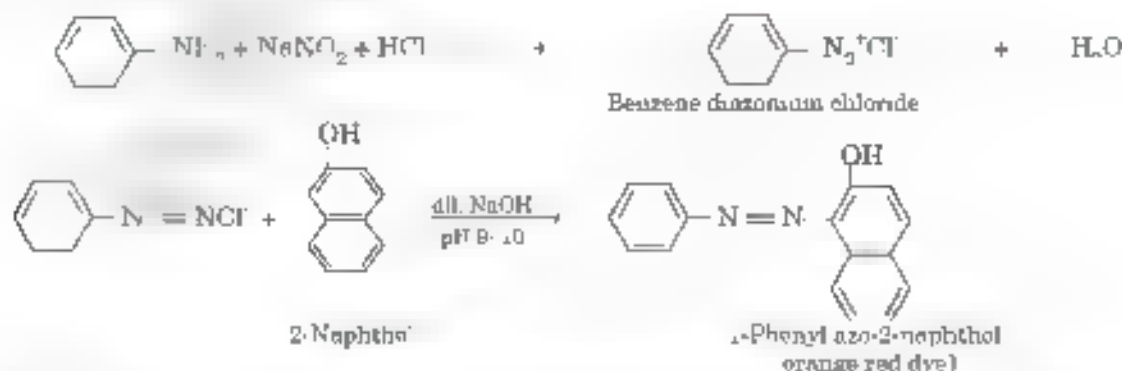
Write the chemical equations involved

D.S.B 2013

Solution

**DISTINCTION BETWEEN PAIRS OF COMPOUNDS****1. Ethylamine and Aniline**

Azo dye test. Dissolve the compound in conc. HCl and add ice-cold solution of HNO_2 ($\text{NaNO}_2 + \text{dil. HCl}$) at 273 K and then treat it with an alkaline cold solution of 2-naphthol. Appearance of brilliant orange or red dye indicates aromatic amine i.e. aniline.



Aliphatic amines i.e. ethylamine does not form dye. It will give brisk effervescence due to the evolution of N_2 but solution remains clear.

2. Ethylamine ($\text{CH}_3\text{CH}_2\text{NH}_2$) and Diethylamine

α-Carbonylamine test. When heated with an alcoholic solution of KOH and CHCl_3 , ethylamine gives foul smelling ethyl isocyanide.



Diethylamine gives N, N-diethylbenzene sulphonamide which is insoluble in aqueous NaOH .



4. Aniline and N-ethylaniline

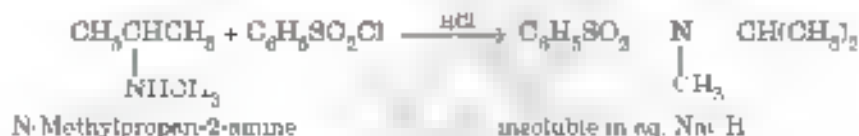
Aniline is a primary amine. Therefore, it gives carbylamine test. When heated with an alcoholic solution of KOH and CHCl_3 , it gives offensive smell of phenylisocyanide.



But, N-ethyl aniline is a secondary amine and hence does not give carbylamine test.

4. N-Methylpropane-2-amine and N-Ethyl N-methylethanolamine

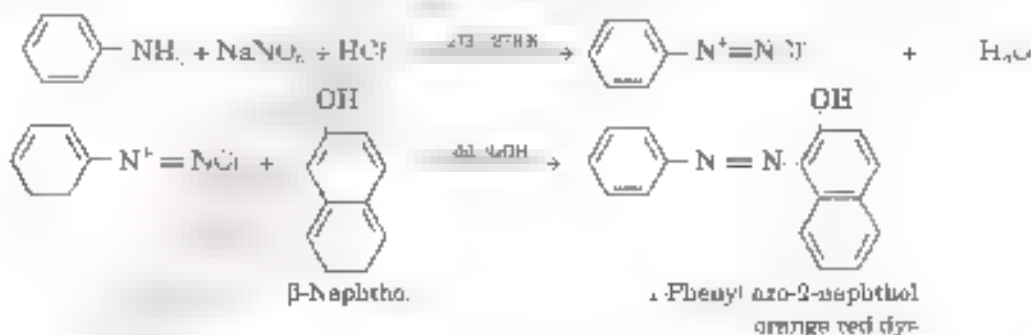
N-methylpropan-2-amine is a secondary amine. On adding H⁺ isberg's reagent, compound formed is insoluble in aqueous NaOH.



But *N*-ethyl-*N*-methylamine does not react with Hinsberg's reagent.

5. Aniline and Benzylamine

Azo dye test: On treatment with excess of $\text{Fe(NO}_3)_3$ + dil. HCl at 278–276 K followed by reaction with an alkaline solution of β -naphthol, amine gives orange-red coloured dye.



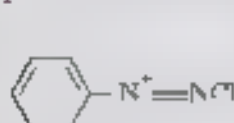
PART B

DIAZONIUM SALTS

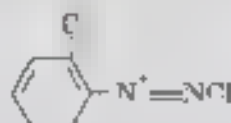
The diazonium salts were discovered by John Peter Weiss in 1858. These have the general formula ArN_2^+X^- , where X^- may be an anion like Cl^- , Br^- , HSO_4^- , BF_4^- , etc. and the group N_2^+ ($\text{N}=\text{N}^+$) is called diazonium group or diazo group. These are obtained when aromatic primary amines react with nitrous acid.

NOMENCLATURE

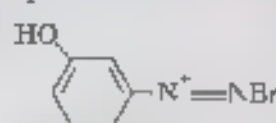
The diazonium salts are named by suffixing the word diazonium to the name of the parent aromatic compound to which they are related followed by the name of the anion. For example,



Benzenediazonium chloride

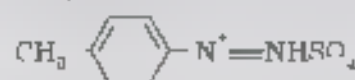


o-Chlorobenzenediazonium chloride

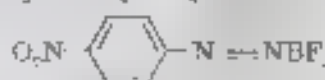


o-Hydroxybenzenediazonium bromide

The diazonium salt may contain other anions also such as NO_3^- , HSO_4^- , BF_4^- etc.



p-Toluenediazonium hydrogen sulphate

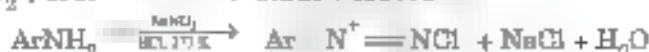
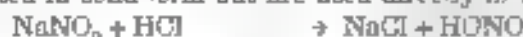


p-Nitrobenzenediazonium fluoroborate

PREPARATION OF DIAZONIUM SALTS

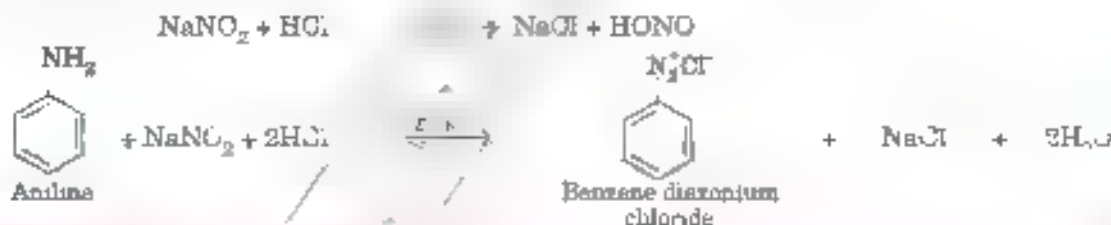
Aromatic diazonium salts are prepared by treating an ice-cold solution of aromatic primary amine in excess of mineral acid like HCl or H_2SO_4 with an ice-cold solution of sodium nitrite dissolved in water. The temperature is maintained between $273\text{--}278\text{ K}$ because most of the diazonium salts decompose at higher temperature.

The diazonium salt so formed remains in the solution. Since the diazonium salts are unstable and explosive substances, they are not isolated in solid form but are used directly in the solution.



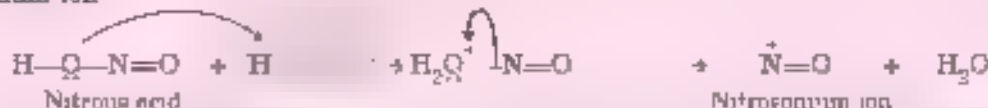
Aromatic amine

For example, benzenediazonium chloride is prepared by treating an ice-cold solution of aniline in hydrochloric acid with an ice-cold solution of sodium nitrite at $0\text{--}5^\circ\text{C}$. The reaction of converting aromatic primary amine to diazonium salt is called **diazotisation**.

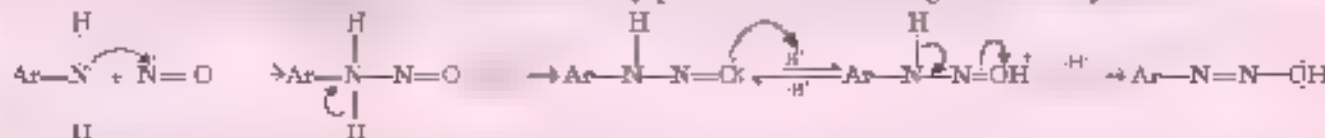


Reaction: Diazotisation of amines

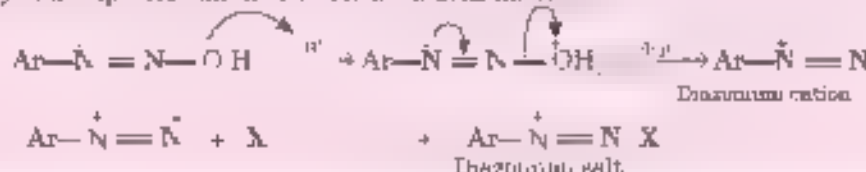
The diazotisation of amines is believed to occur by the following mechanism. Nitrous acid formed by the reaction of sodium nitrite and mineral acid, takes up a proton from the acid and undergoes heterolysis to form nitrosonium ion.



The electrophilic nitrosonium ion reacts with the nitrogen of the amine and coordinates with the lone pairs of electrons at N to form N-nitroso derivative, which by protonic shift rearranges to diazonylhydroxide.

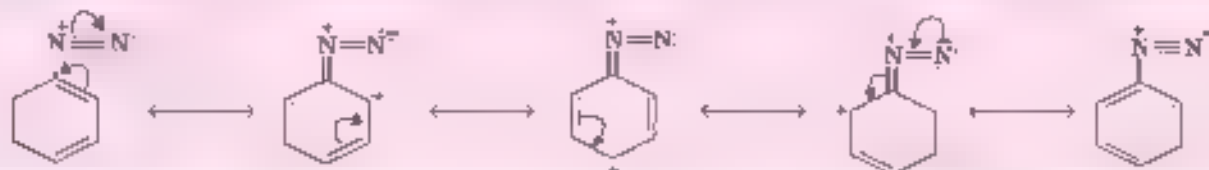


The diazonylhydroxide in acidic solution takes up a proton and by the elimination of water molecule forms diazonium ion, which may take up acid anion X to form benzenediazonium salt.



Stability of Diazonium salt

Aromatic diazonium salts are stable due to the dispersal of positive charge over the benzene ring as shown below:

**R U Curious...****Are primary aliphatic diazonium salts formed?**

➤ Primary aliphatic diazonium salts are highly unstable alkane diazonium salts. These readily decompose even at low temperature (273–278 K) forming carbocation and nitrogen gas.

**Why is it important to keep the temperature very low (273–278 K) during the formation of diazonium salts?**

➤ Aromatic diazonium salts are formed only in ice cold solution (273–278 K). However, if temperature is more than 278 K amines form phenol with the evolution of N_2 gas.

**PHYSICAL PROPERTIES OF DIAZONIUM SALTS**

The general physical properties of diazonium salts are

1. Diazonium salts are generally colourless, crystalline solids.
2. These are readily soluble in water and are stable in cold but react with water when warmed. They are less soluble in alcohol.
3. They are unstable and explode in dry state. Therefore, they are generally used in solution state.
4. Certain diazonium salts such as fluorobenzenediazonium are water insoluble and are stable enough to be dried and stored.
5. Their aqueous solutions are neutral in nature and conduct electricity due to the presence of ions.

CHEMICAL PROPERTIES OF DIAZONIUM SALTS

The reactions of benzene diazonium salts can be broadly divided into two types

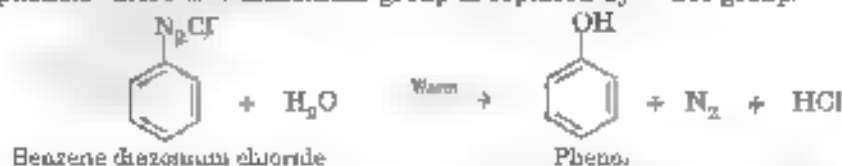
A. Reactions involving displacement of diazo group

B. Reactions involving retention of diazo group

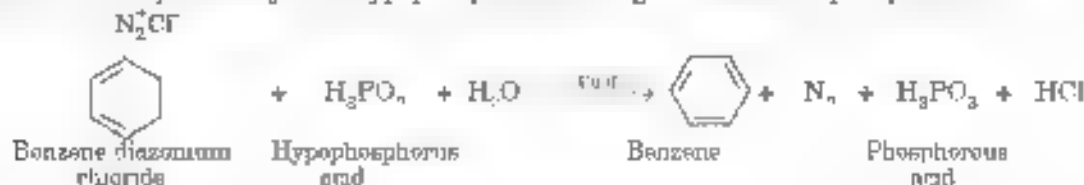
A. Reactions involving displacement of nitrogen

Diazo group being a very good leaving group, is readily substituted or replaced by other groups. In these reactions, nitrogen of diazonium salts is lost as N_2 and different groups are introduced in its place. Some of the important replacement reactions are

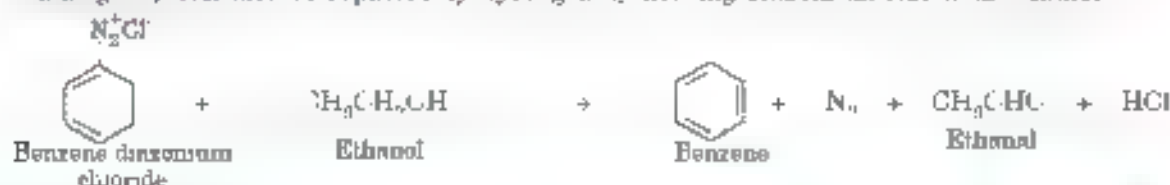
(i) **Replacement by $-\text{OH}$ group.** When an aqueous solution of diazonium salt is boiled upto 283 K or steam distilled, it gives phenols. Here, the diazonium group is replaced by $-\text{OH}$ group.



(ii) **Replacement by hydrogen or deamination.** When diazonium salt is treated with mild reducing agents such as hypophosphorous acid (phosphinic acid) i.e. H_3PO_2 in the presence of this salt as a catalyst at room temperature benzene is obtained preferably. The hypophosphorous acid gets oxidised to phosphorous acid.

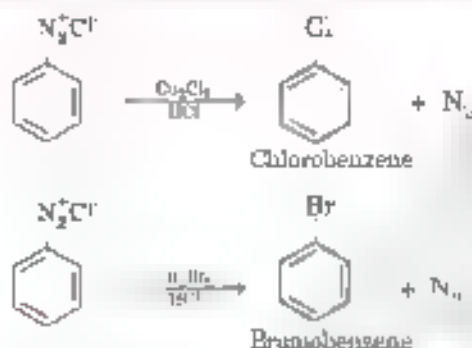


The diazo group can also be replaced by hydrogen by heating diazonium salt with ethanol.



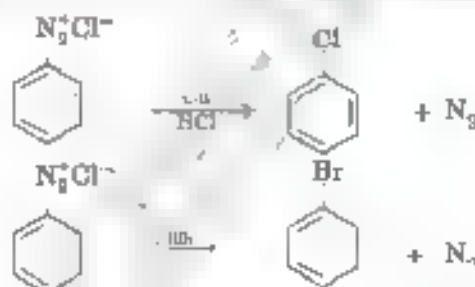
This complete process involving the substitution of an aryl group followed by reduction of the diazonium salt or replacement of the diazo group by hydrogen is called **deamination**.

(iii) **Replacement by Cl and Br group.** When a diazonium salt solution is warmed with cuprous chloride in hydrochloric acid or cuprous bromide in hydrobromic acid the corresponding halide is formed.



This reaction is called **Sandmeyer reaction**.

When the diazonium salt solution is warmed with copper powder and the corresponding hydrogen acid, the respective halogen is introduced. The reaction is a modified form of Sandmeyer reaction and is known as **Gattermann reaction**.



Gattermann reaction is modification of Sandmeyer reaction.

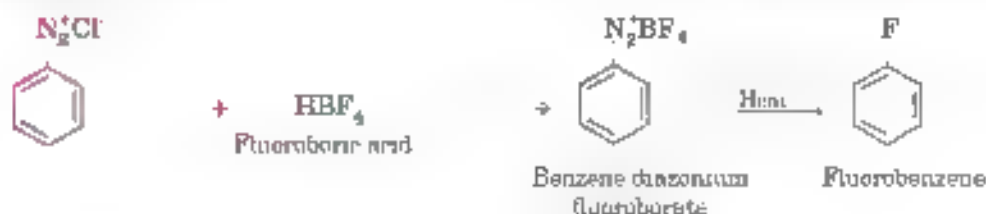
The yield of Sandmeyer reaction is found to be better than Gattermann reaction.

(iv) **Replacement by iodo (-I) group.** When aqueous solution of benzene diazonium salt is warmed with excess of potassium iodide, aryl iodide is formed.



Iodine is not easily introduced into the benzene ring directly therefore, this reaction provides an indirect method for preparing iodo compounds.

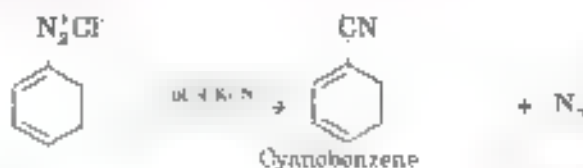
(v) **Replacement by fluoro (-F) group.** When diazonium salt is treated with fluoroboric acid HBF_4 , benzene diazonium fluoroborate is precipitated, which on heating decomposes to fluorobenzene. This reaction is called **Balz-Schiemann reaction**.



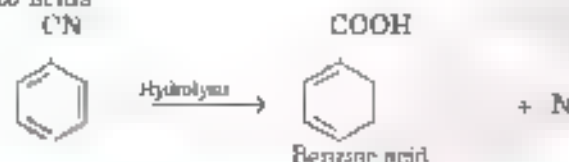
NOTE

The preparation of aryl halides from diazonium salts is a good method and has many advantages. Aryl chlorides and bromides when obtained by direct iodination of aromatic compounds give mixtures of products which are difficult to separate. However in the diazonium salt replacement method, a pure single product is formed. This also provides good synthetic route for the preparation of aryl iodides and fluorides which are not obtained by direct iodination.

(i), Replacement by cyano (-CN) group. When benzene diazonium salt is treated with copper cyanide dissolved in aqueous KCN, cyanobenzene is formed.

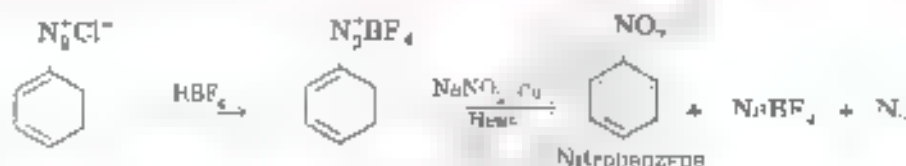


The nitriles can be hydrolysed to acids

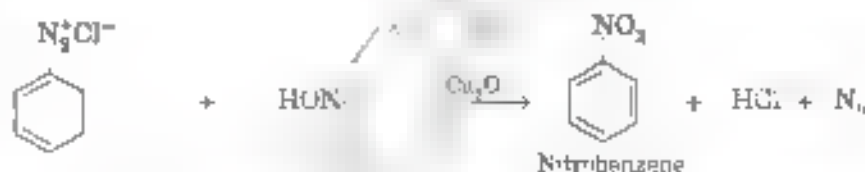


The method of preparing carboxylic acids is more useful than carbonylation of Grignard reagents.

(ii) Replacement by nitro (-NO₂) group. Nitrobenzene is prepared by heating diazonium fluoroborate with aqueous NaNO₂ in the presence of copper powder



Alternative y nitro compounds may be prepared by treating diazonium salt with nitrous acid in the presence of cuprous oxide.



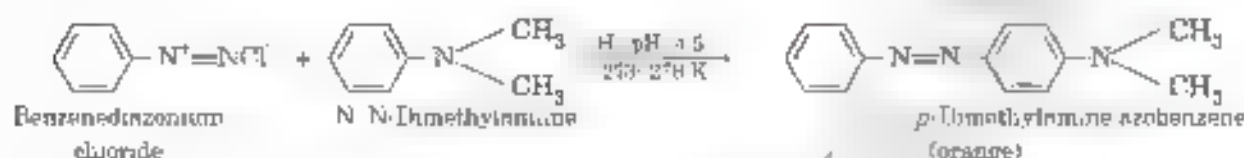
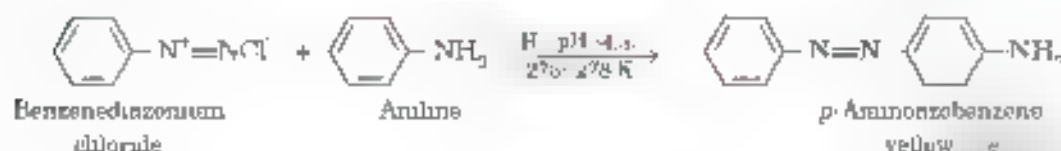
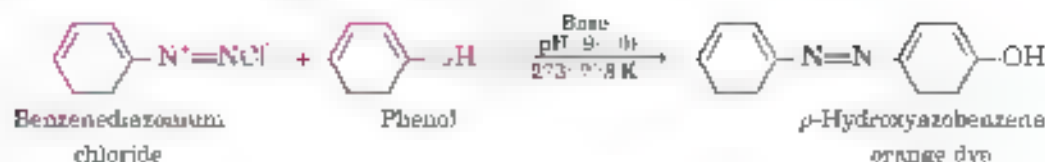
(iii) Replacement by thio (-SH) group. When diazonium salt is treated with potassium hydrosulphide, thiophenol is produced.



B. Reactions involving retention of diazo group

Coupling reactions: Benzene diazonium salts react with highly reactive (i.e. electron rich) aromatic compounds such as phenols and amines to form azo compounds. Ar-N=N-Ar'. The reaction is known as **coupling reaction**. These azo compounds are generally coloured and are used as dyes. The colour of azo compounds is due to extended conjugate system involving the double bond of both the aromatic rings through -N=N- double bond.

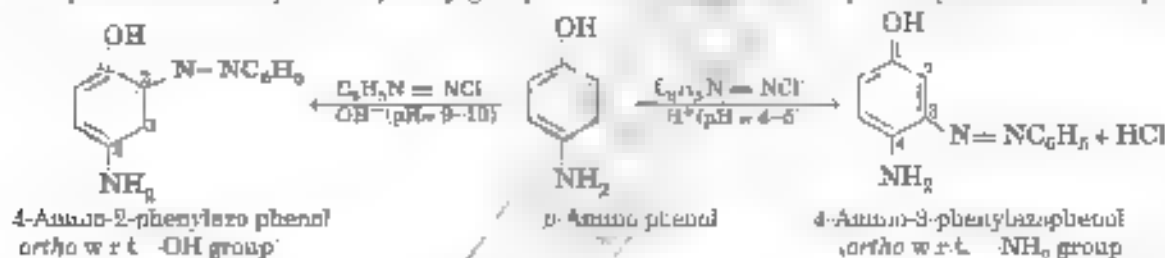
It may be noted that coupling with phenol occurs in basic medium (pH = 9-10) while that of amines occurs in faintly acidic medium (pH = 4-5) at 273-278 K. The coupling reaction is an example of **electrophilic substitution reaction** in which the diazonium cation with a positive charge on the terminal nitrogen acts as the electrophile and the electron rich compounds such as phenols and amines act as nucleophiles.



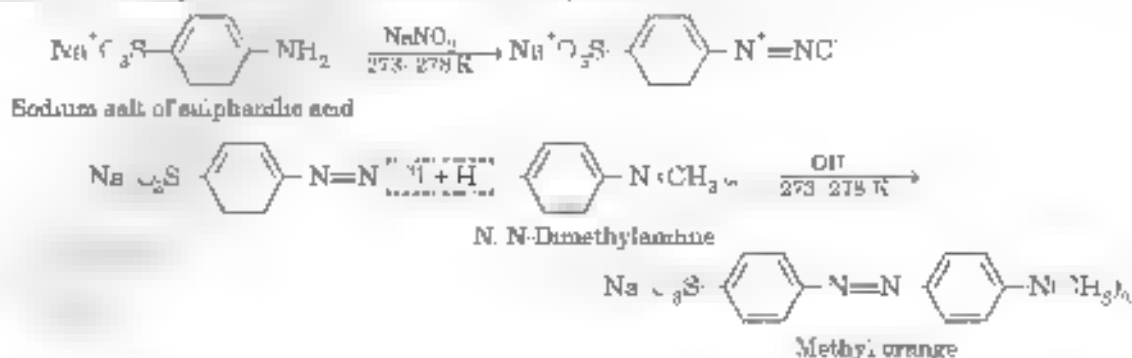
Coupling occurs *para* to hydroxy or amino group. However if the *para* position is blocked with respect to hydroxy or amino group it occurs at *ortho* position. For example,



In case of aromatic compounds containing both hydroxy or amino groups the coupling occurs in the alkaline medium at *p*- or *o*-position with respect to hydroxy group and in acidic medium at *p*- or *o*-position with respect to amino group.



All azo compounds are strongly coloured and are used as dyes. Methyl orange is an important dye obtained by coupling the diazonium salt of sulphamic acid with *N,N*-dimethylaniline.



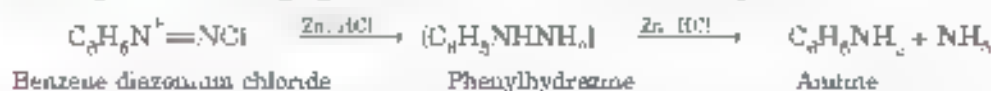
11 Reduction to arylhydrazines: Arene diazonium salts are reduced to aryl hydrazines upon treatment with stannous chloride and hydrochloric acid or zinc dust and acid or sodium sulphide or even by electrostatic method.



Phenyldiazine, which is an important reagent for organic synthesis can be easily prepared in good yield from benzenediazonium chloride as



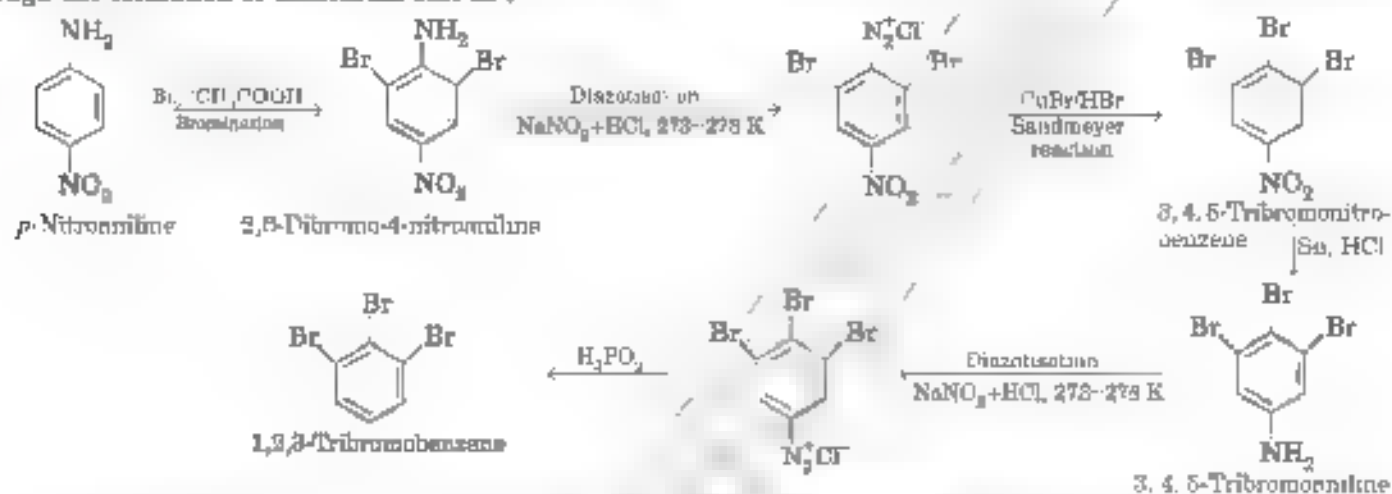
However, if vigorous reducing agent such as Zn/HCl is used the product is aromatic amine.



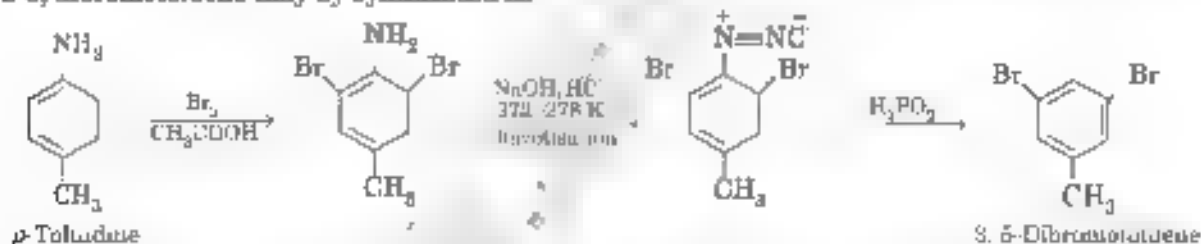
IMPORTANCE OF BENZENE DIAZONIUM SALTS IN SYNTHETIC ORGANIC CHEMISTRY

Diazonium salts are highly useful intermediates in the synthesis of large variety of aromatic compounds. Therefore these are regarded as good synthetic tools in the hands of a chemist. These can be used to prepare many classes of organic compounds especially aryl halides in pure state. Some common examples are

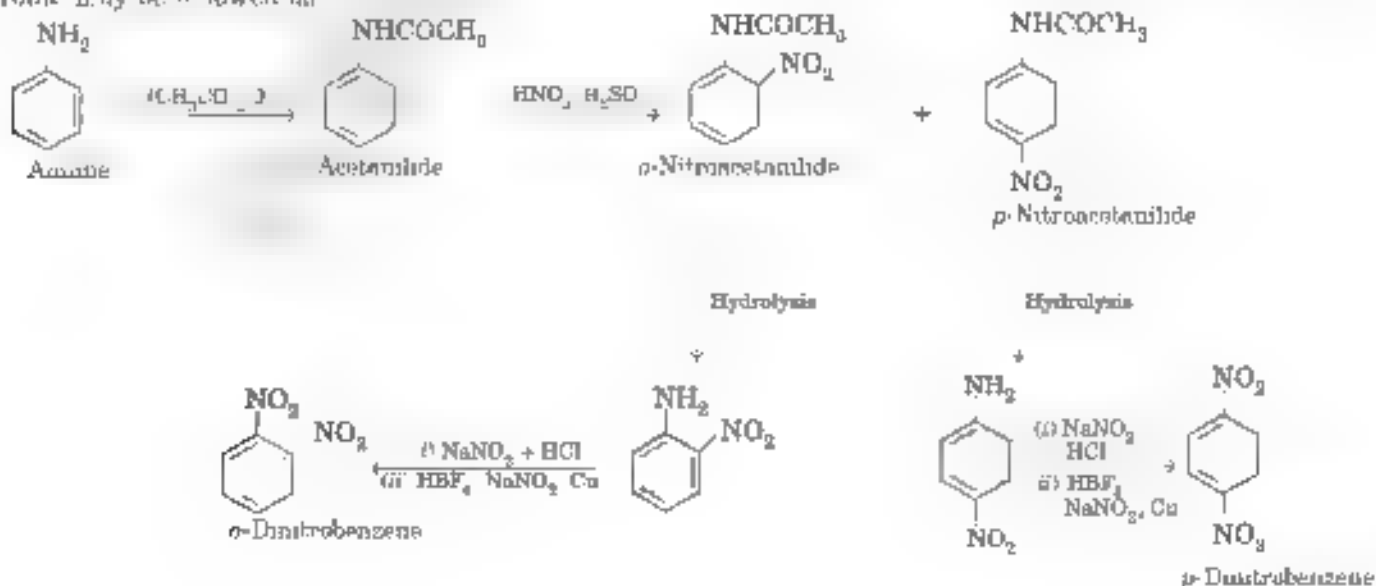
1. Synthesis of 1, 2, 3-tribromo benzene. 1, 2, 3-tribromo benzene is not formed in the pure stage by direct bromination of benzene. However, it can be prepared by the following sequence of reactions starting from *p*-nitroaniline through the formation of diazonium salt as,



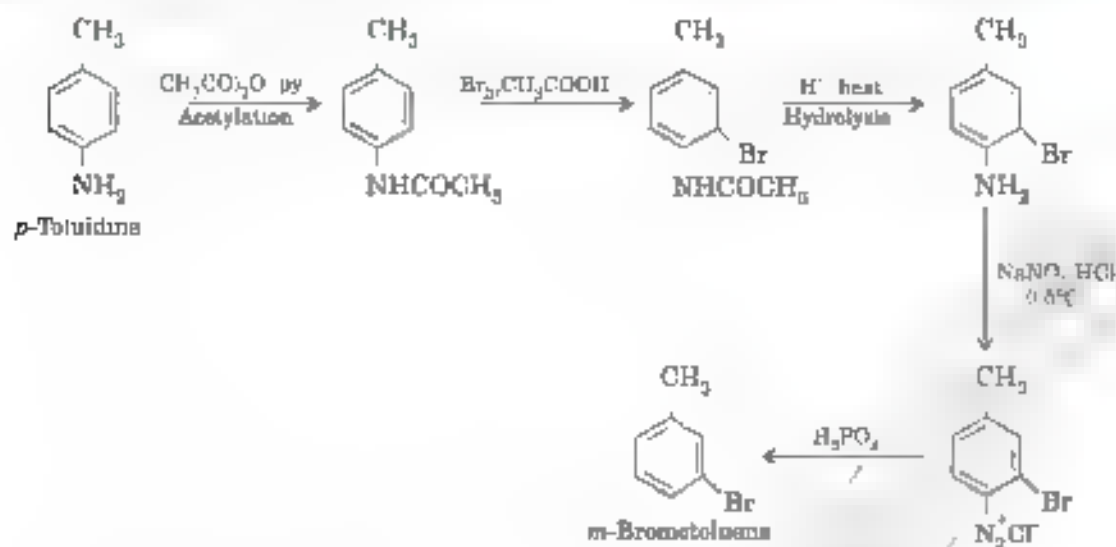
2. Synthesis of 3, 5-dibromotoluene. Direct bromination of toluene with $\text{Br}_2/\text{FeBr}_3$ gives 2, 4-dibromotoluene. But 3, 5-dibromotoluene may be synthesised as



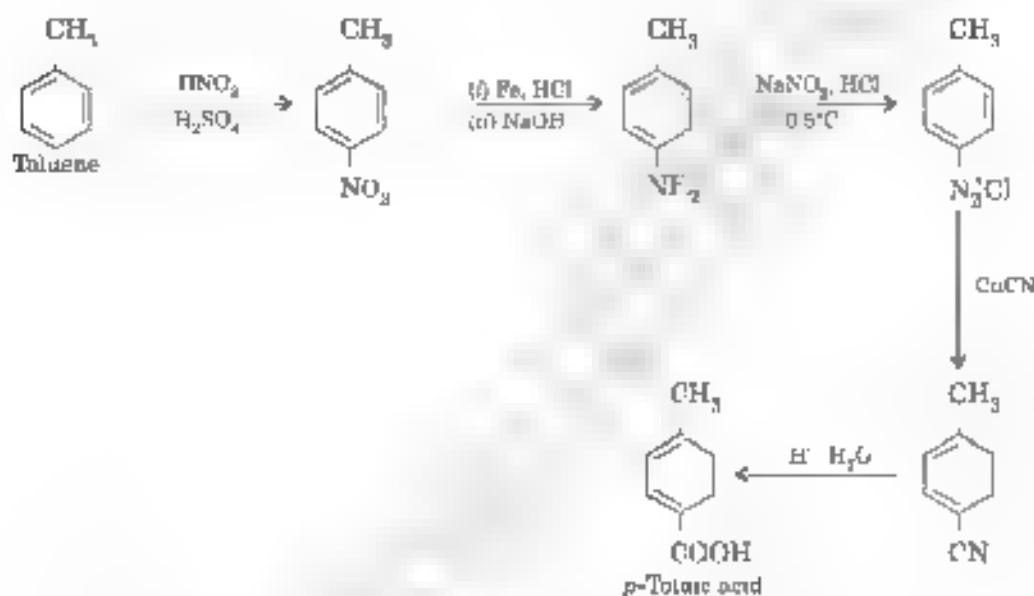
3. Synthesis of *o*- and *p*-dinitrobenzenes. These cannot be prepared by direct substitution. However, diazonium salts route may be followed as



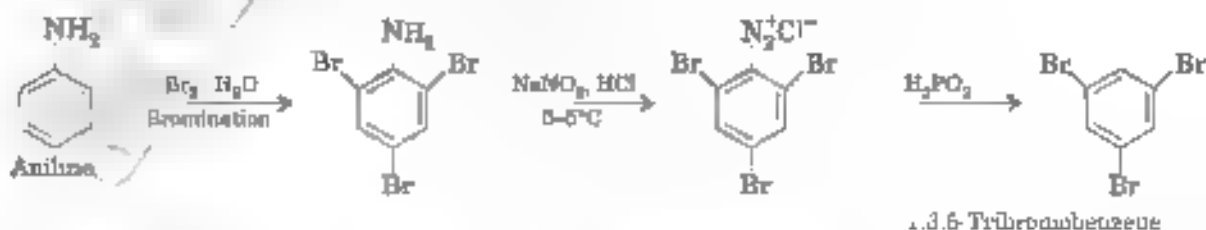
4. Synthesis of *m*-bromotoluene. It cannot be prepared by direct bromination of toluene or Friedel Crafts alkylation of bromobenzene because of *o*, *p*-directing nature of methyl group. It can be synthesized as



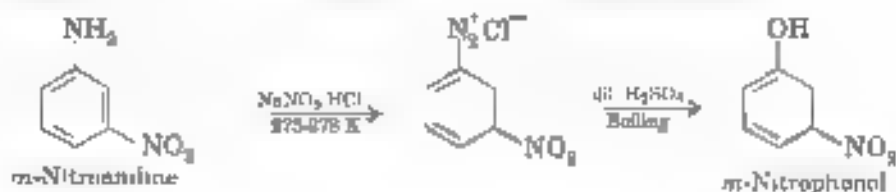
5. Synthesis of *p*-toluic acid. This can be synthesized as ,



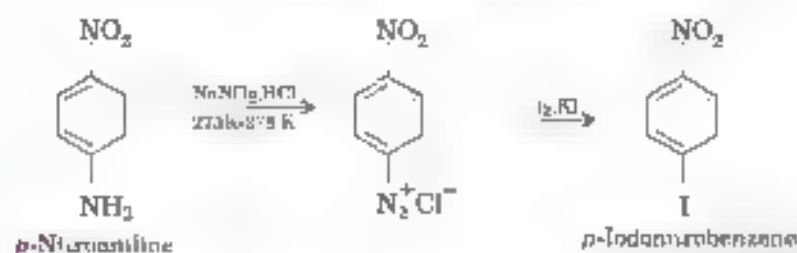
6. Synthesis of 1,3,5-tribromobenzene. It can be synthesized as



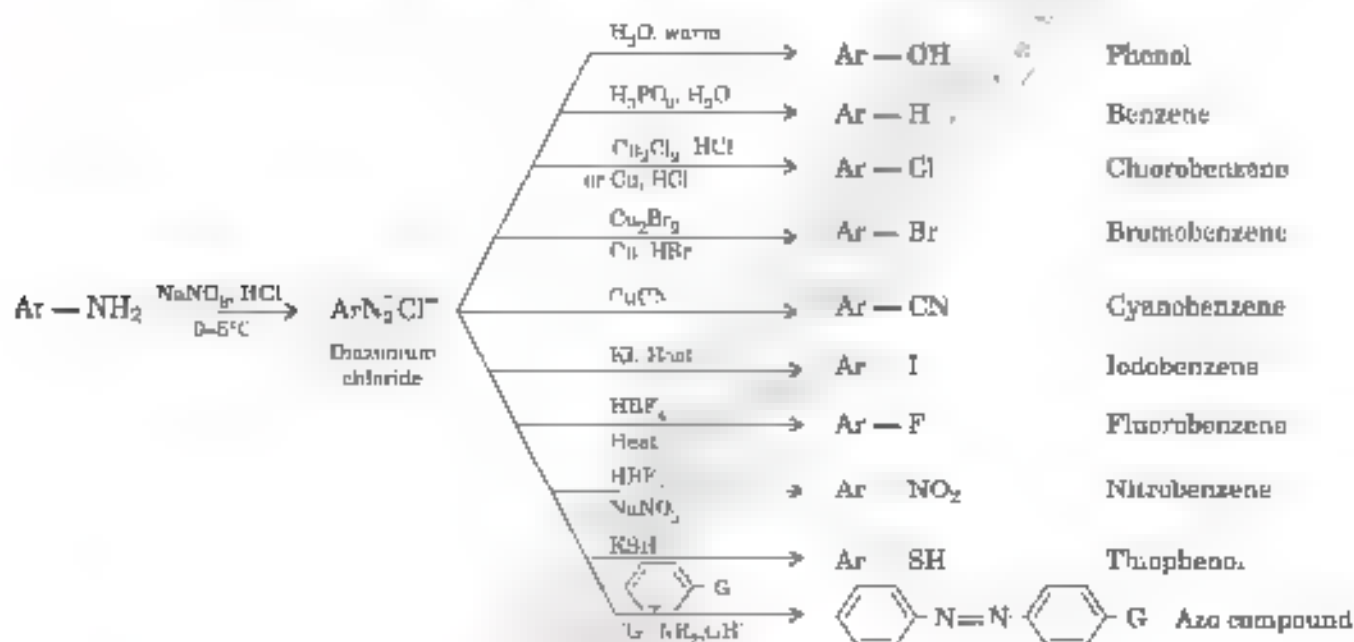
7. Synthesis of *m*-nitrophenol from *m*-nitroaniline. It can be synthesized as



B. Synthesis of *p*-iodonitrobenzene. It can be synthesised from *p*-nitroaniline as



Some of the important chemical reactions and the important products formed are summarized below



Uses of diazonium salts. Diazonium salts are used

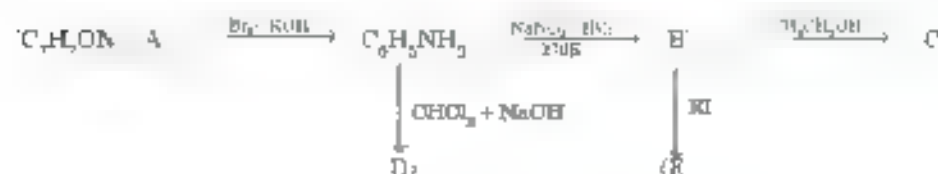
1. for the manufacture of azo dyes.
2. for the industrial preparation of important organic compounds like *m*-bromotoluene, *m*-bromophenol, etc.
3. for the preparation of a variety of useful halogen substituted arenes.

PROBLEM SOLVING EXAMPLES

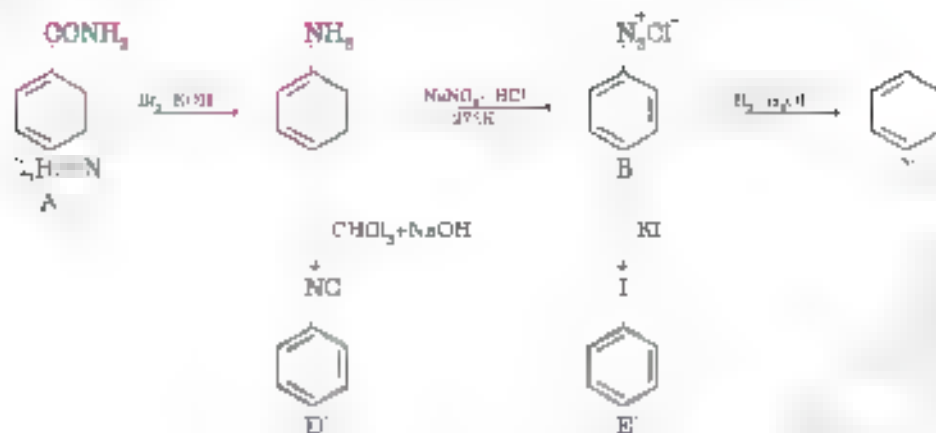
Example 12.

An aromatic compound **A** of molecular formula $\text{C}_6\text{H}_5\text{ON}$ undergoes a series of reactions as shown below. Write the structures of **A**, **B**, **C**, **D** and **E** in the following reactions.

D.S.B. 2016



Solution

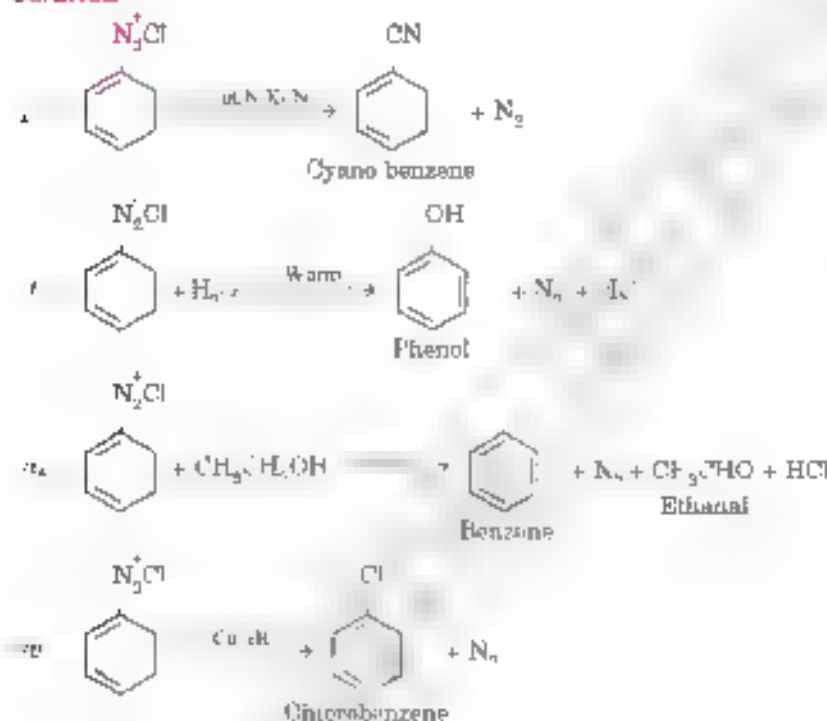


Example 13.

Write the main products when benzene diazonium chloride ($C_6H_5N_2^+Cl^-$) reacts with the following.

- (i) $CuCN/KCN$ (ii) H_2O (Pb S.B. 2018) (iii) CH_3CH_2OH (AI S.B. 2015, 2018)
 (iv) Copper powder/HCl (Pb.S.B. 2016)

Solution



Example 14.

How will you convert

- (a) propionamide to ethylamine
 (b) aniline to phenol
 (c) *p*-toluidine into 2-bromo-4-methylaniline
 (d) aniline to acetanilide
 (e) aniline to benzene
 (f) aniline to bromobenzene
 (g) aniline into benzonitrile
 (h) methylamine to ethylamine

HP S.B. 2016)

Tripura S.B. 2016)

HP S.B. 2016)

Pb. S.B. 2016)

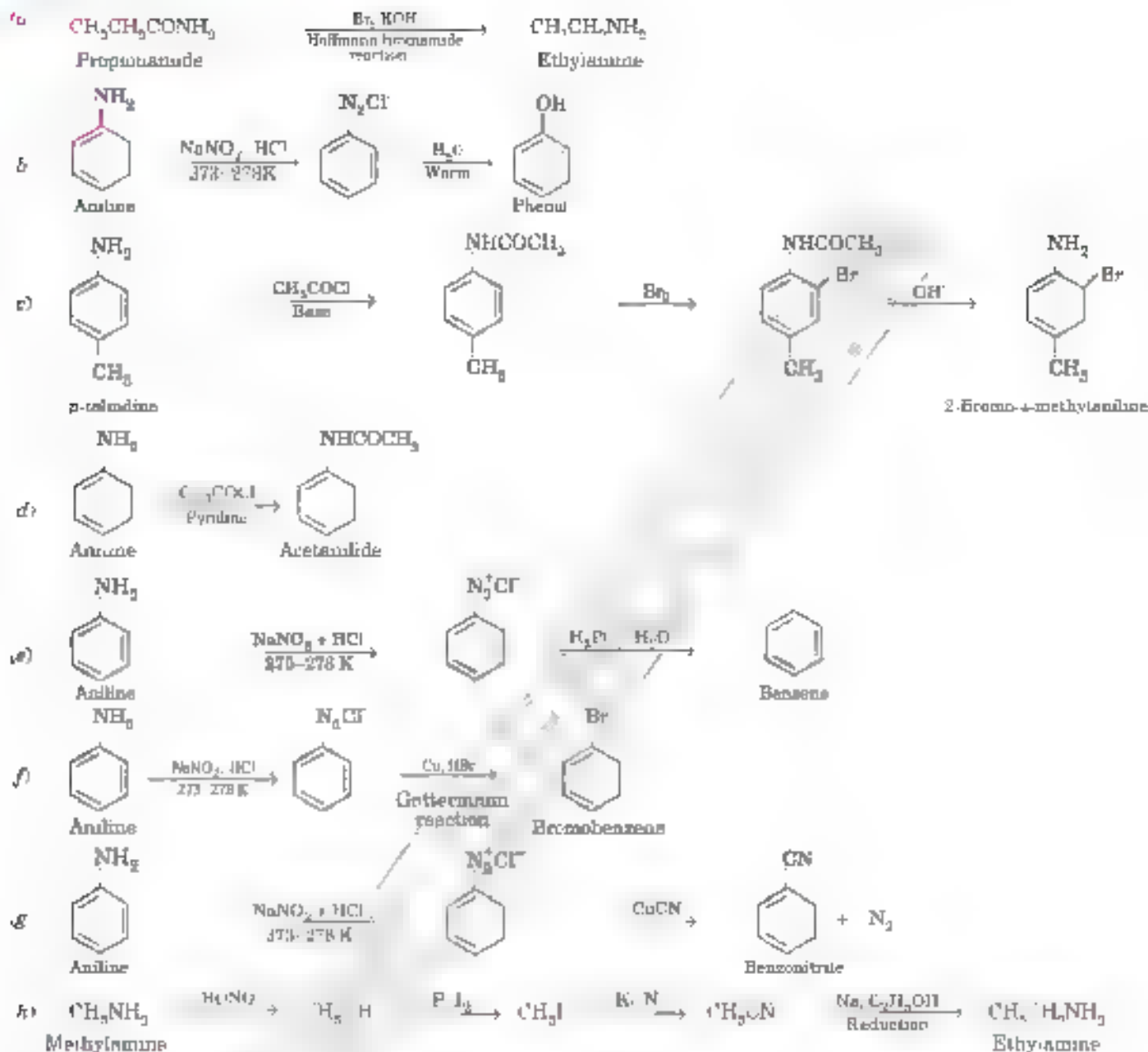
HP S.B. 2016)

HP S.B. 2016)

(Pb.S.B. 2016)

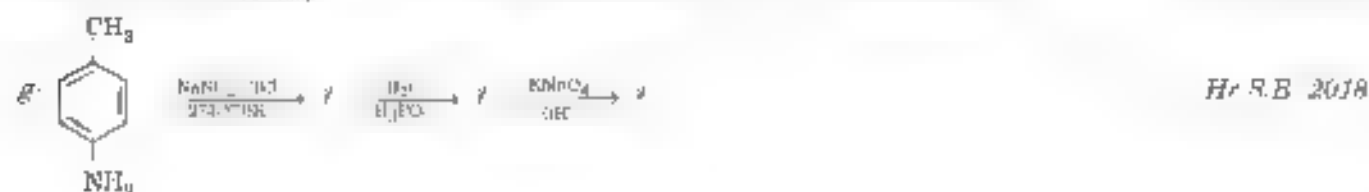
HP S.B. 2015, 2016)

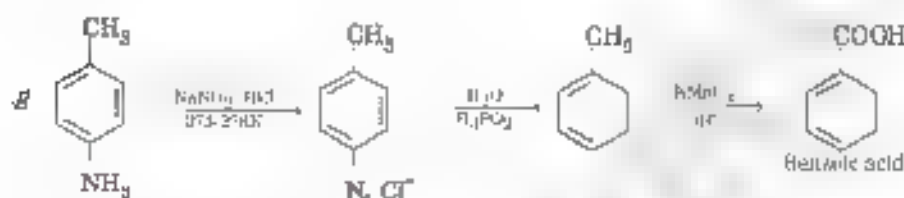
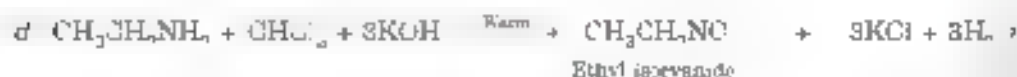
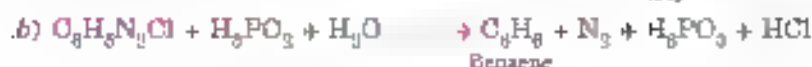
Solution



Example 16.

Complete the following chemical equations



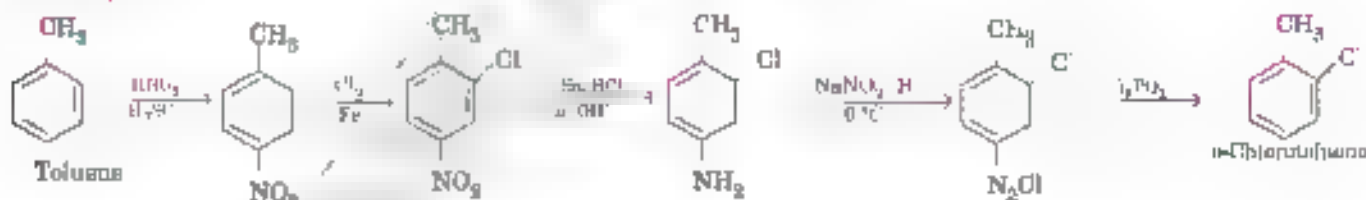


Example 10.

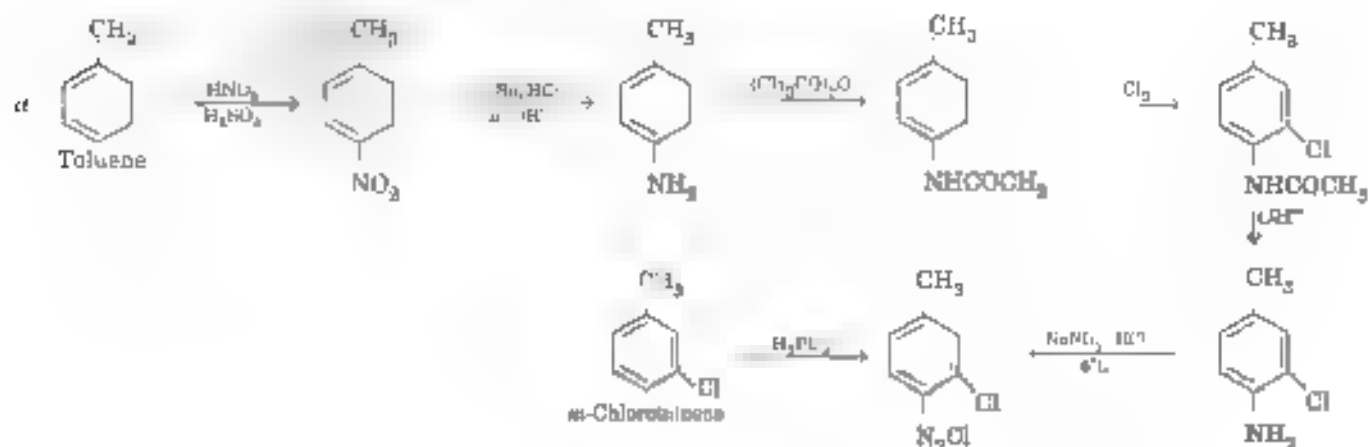
Starting from toluene prepare

m-chlorotoluene + m-chlorotoluene + p-chlorotoluene + p-cyanotoluene + $\text{p-cyanobenzoic acid}$

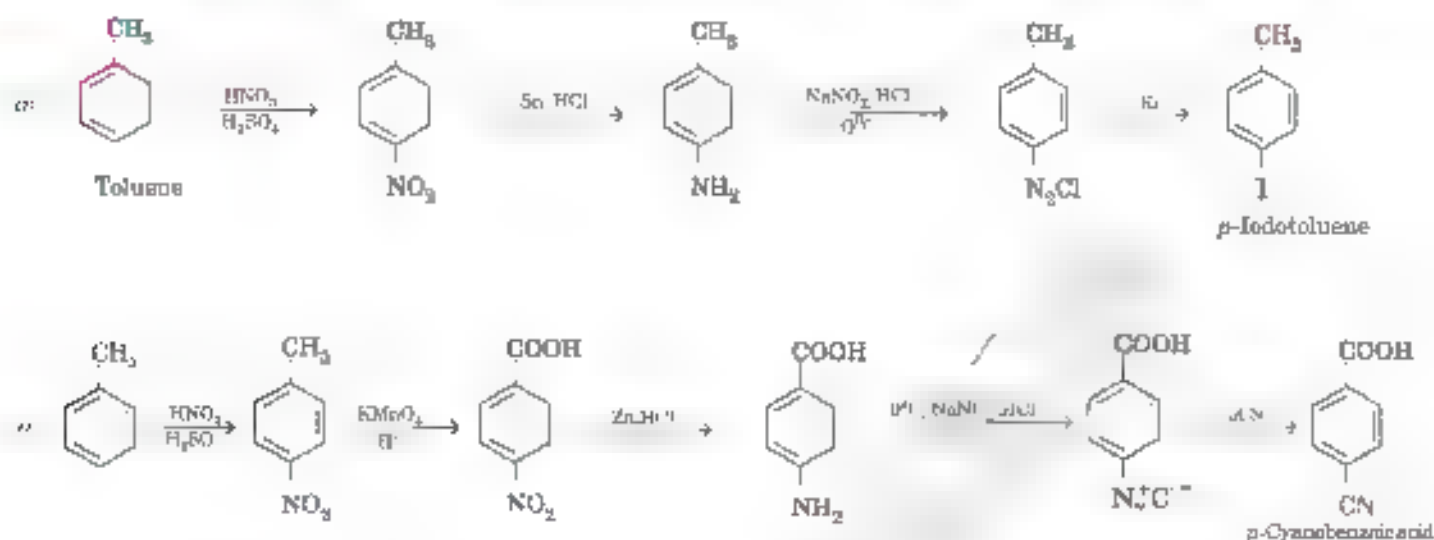
Solution.



In this case, the *para* position is blocked by NO_2 to prepare only *ortho* product.



The NHCOCH_3 group helps Cl to orient at ortho position, which is meta to CH_3 . It is then removed.

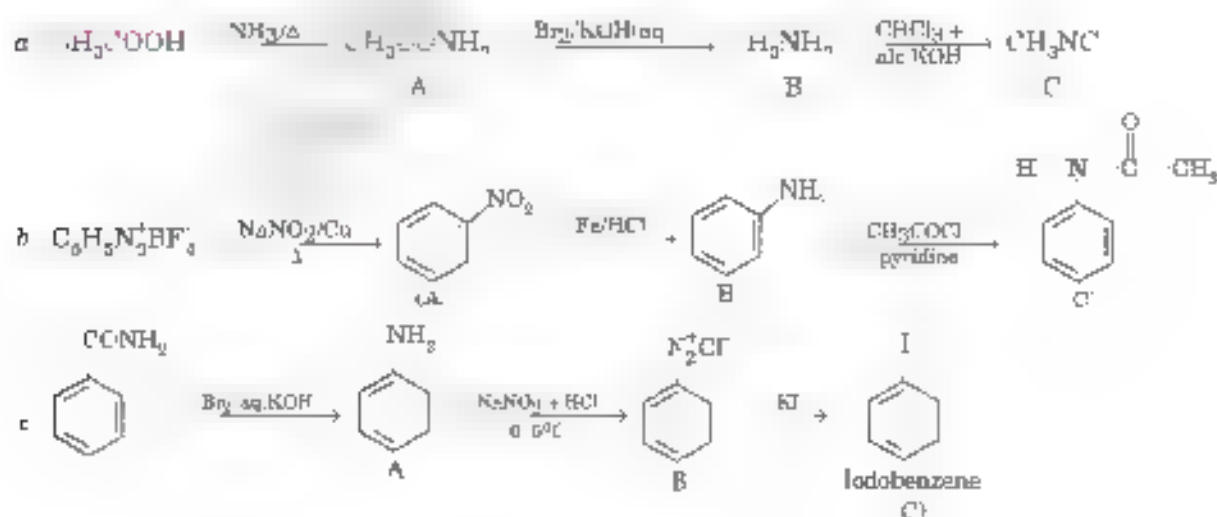


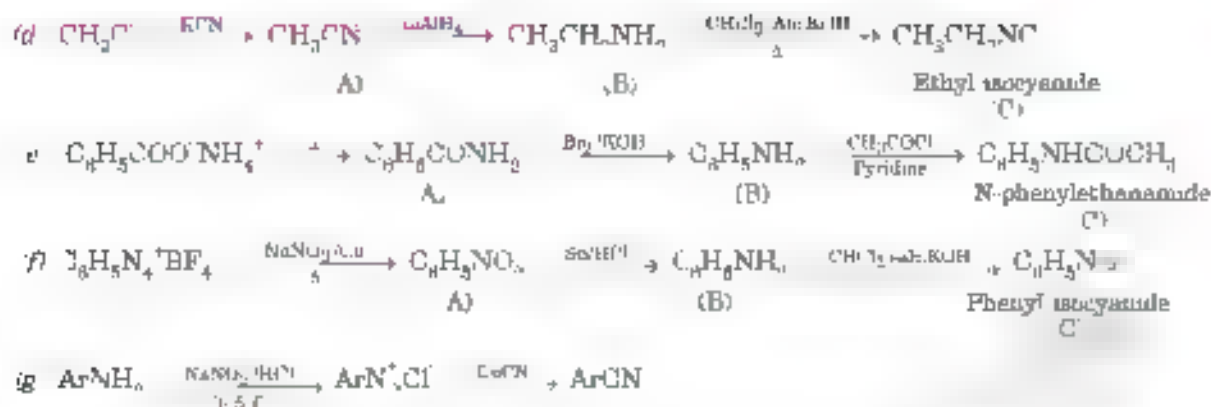
Example 17

Give the structures of A, B and C in the following reactions

- a) $\text{CH}_3\text{COOH} \xrightarrow{\text{NH}_3/\Delta} \text{A} \xrightarrow{\text{Br}_2/\text{KOH(aq)}} \text{B} \xrightarrow{\text{CHCl}_3 + \text{alc KOH}} \text{C}$ A.I.S.B 2017
- b) $\text{C}_6\text{H}_5\text{N}^+\text{BF}_4^- \xrightarrow[\Delta]{\text{NaNO}_2/\text{Cu}} \text{A} \xrightarrow{\text{Fe/HCl}} \text{B} \xrightarrow[\text{pyridine}]{\text{CH}_3\text{COCl}} \text{C}$ A.I.S.B 2017
- c) $\text{C}_6\text{H}_5\text{CONH}_2 \xrightarrow{\text{Br}_2, \text{aq. NaOH}} \text{A} \xrightarrow[\text{D.F.C.}]{\text{NaNO}_2/\text{HCl}} \text{B} \xrightarrow{\text{KI}} \text{C}$ D.S.B 2016
- d) $\text{CH}_3\text{Cl} \xrightarrow{\text{KCN}} \text{A} \xrightarrow{\text{LiAlH}_4} \text{B} \xrightarrow[\Delta]{\text{CHCl}_3, \text{alc KOH}} \text{C}$ D.S.B 2016
- e) $\text{C}_6\text{H}_5\text{COONH}_4^+ \xrightarrow{\Delta} \text{A} \xrightarrow{\text{Br}_2/\text{KOH}} \text{B} \xrightarrow[\text{Pyridine}]{\text{CH}_3\text{COCl}} \text{C}$ A.I.S.B 2016
- f) $\text{C}_6\text{H}_5\text{N}^+\text{BF}_4^- \xrightarrow[\Delta]{\text{NaNO}_2/\text{Cu}} \text{A} \xrightarrow{\text{Al/HCl}} \text{B} \xrightarrow[\text{alc KOH}]{\text{CHCl}_3} \text{C}$ A.I.S.B 2016
- g) $\text{ArNH}_2 \xrightarrow[\text{0-5}^\circ\text{C}]{\text{NaNO}_2/\text{HCl}} \text{A} \xrightarrow{\text{C}_6\text{H}_5\text{NH}_2} \text{B}$ Majoram S.B 2018

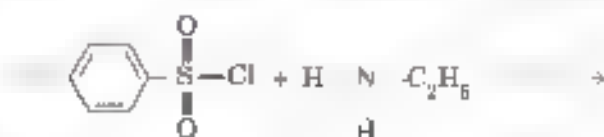
Solution



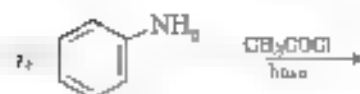


Example 18.

(a. Write the products of the following reactions



Hr S.B. 2016.



A.I.S.B. 2016, H.P.S.B. 2016.



Kolkata S.B. 2016)



Kolkata S.B. 2016



Jharkhand S.B. 2016)

(b) How will you convert

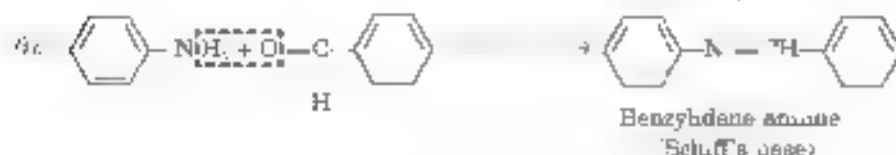
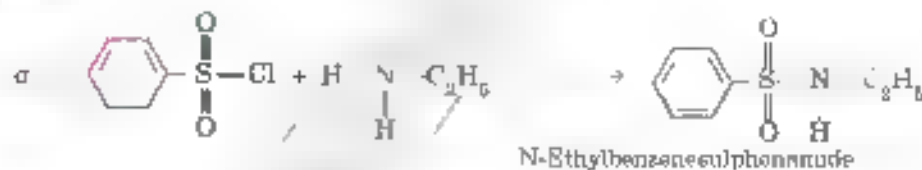
benzene to aniline

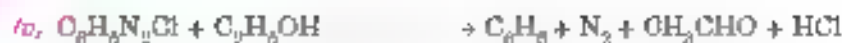
H.P.S.B. 2016)

(c) benzoic acid to aniline

(H.P.S.B. 2016)

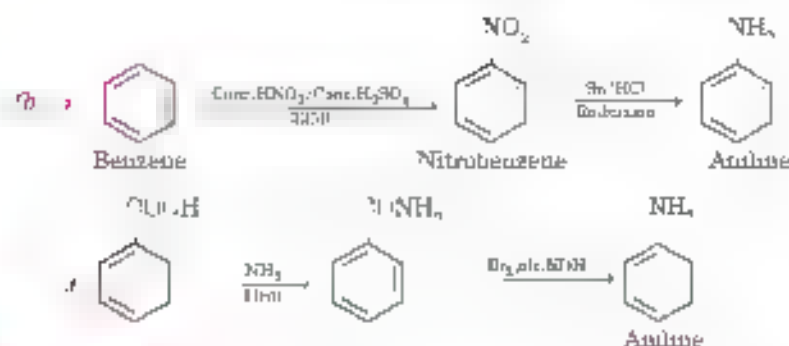
Solution





Benzene

Ethanal

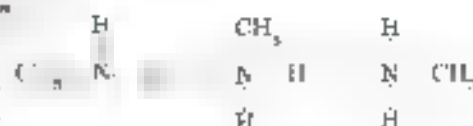


add on

Conceptual Questions

Q.1. Why does methylamine has lower boiling point than methanol ?

Ans. Methylamine is polar and can form intermolecular hydrogen bonds. However, its tendency to form intermolecular hydrogen bonds is less than that of methanol CH_3OH which has highly electronegative oxygen atom. As a result, CH_3NH_2 has lower boiling point than CH_3OH .



Q.2. Why is methylamine stronger base than ammonia ?

Ans. Both ammonia and CH_3NH_2 have a lone pair of electrons and therefore, behave as Lewis bases. The alkyl group in CH_3NH_2 has + I inductive effect and is electron releasing in nature. As a result, its electron releasing tendency becomes more. Thus, CH_3NH_2 is more basic than ammonia.

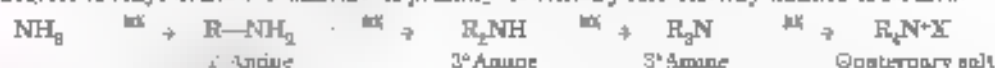
Q.3. Aniline dissolves in aqueous HCl. Why ?

Ans. Aniline dissolves in aqueous HCl due to the formation of water soluble salt.



Q.4. Why is it difficult to prepare pure amines by ammonolysis of alkyl halides ?

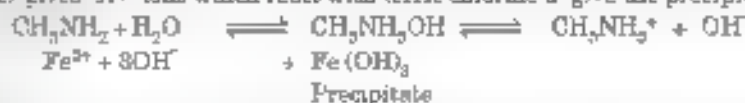
Ans. By ammonolysis of alkyl halides a mixture of primary, secondary and tertiary amines is formed.



The separation of these amines is very difficult. Thus, it is very difficult to prepare pure amines by ammonolysis of alkyl halides.

Q.5. Methylamine in water reacts with ferric chloride to precipitate ferric hydroxide. Explain.

Ans. Methylamine in water gives OH^- ions which react with ferric chloride to give the precipitate of ferric hydroxide as



Q.6. Electrophilic substitution in case of aromatic amines takes place more readily than benzene. Explain.

Ans. NH_2 group in aromatic amines strongly activates the aromatic ring through delocalisation of the lone pair of electrons on N-atom over the aromatic ring. However, no such delocalisation occurs in case of benzene.

Q.7. Although boron trifluoride adds on trimethylamine but it does not add on triphenylamine. Explain.

Ans. Trimethylamine has three electron donating alkyl groups and therefore acts as a Lewis base and reacts with BF_3 a Lewis acid.



On the other hand, in triphenylamine, the lone pair of N gets delocalised over three benzene rings. Thus, the lone pair is not readily available to BF_3 for reaction.

Q.8. Why does silver chloride dissolve in methylamine solution?

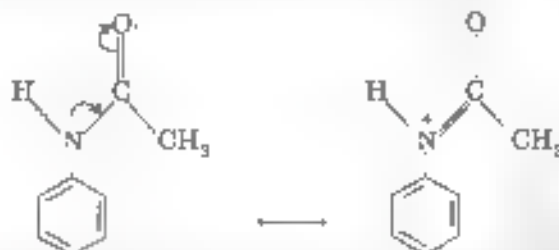
Ans. Silver chloride dissolves in methylamine solution because it forms soluble complex



Q.9. Why does the reactivity of NH_2 get reduced in acetanilide?

(Pb. S.B. 2018)

Ans. In acetanilide, the amide group withdraws electrons from NH_2 group as shown below



As a result the electron pair on nitrogen gets displaced to the carbonyl group. Therefore the unshared pair of electrons on nitrogen is less available for donation to the aromatic ring. Consequently the electron density at *ortho* and *para* position in the benzene ring gets reduced which in turn results in reduced reactivity towards electrophilic substitution of benzene.

Q.10. Although trimethyl amine and *n*-propylamine have the same molecular mass, the former boils at a lower temperature (276 K) than the latter (323 K). Why?

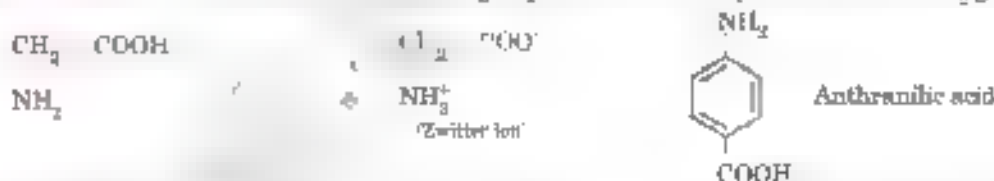
Ans. *n*-Propylamine $\text{CH}_3(\text{CH}_2)_2\text{NH}_2$ has two hydrogen atoms on the nitrogen atom and therefore forms intermolecular hydrogen bonding. Hence, its boiling point is high. In the other hand, trimethylamine, $(\text{CH}_3)_3\text{N}$ does not have hydrogen atom on the nitrogen atom. As a result, it does not undergo hydrogen bonding and hence its boiling point is low.

Q.11. Sulphanilic acid is soluble in dil. NaOH but not in dil. HCl . Explain.

Ans. Sulphanilic acid exists as a zwitter ion, $\text{NH}_3^+ \text{C}_6\text{H}_4 \text{SO}_3^-$. In the presence of dil. NaOH , the weakly acidic NH_3^+ group transfers its H^+ to OH^- to form a soluble $p\text{-NH}_2\text{C}_6\text{H}_4\text{SO}_3\text{Na}$. On the other hand, SO_3^- group is very weak base and therefore does not accept a proton from dil. HCl to form $p\text{-NH}_3^+\text{C}_6\text{H}_4\text{SO}_3\text{H}$. Hence, it does not dissolve in dil. HCl .

Q.12. Glycine exists as $\text{NH}_3^+ \text{CH}_2\text{COO}^-$, zwitter ion but anthranilic acid (*p*-amino benzoic acid) does not exist as zwitter ion. Why?

Ans. Glycine exists as zwitter ion because the acidic group COOH donates proton to basic NH_2 group as



However, in anthranilic acid, the electron withdrawing benzene ring suppresses the tendency of a weak acidic group COOH to transfer its proton to NH_2 group.

Q.13. Tertiary amines do not undergo acylation. Explain.

(Pb. S.B. 2014, H.P. S.B. 2016)

Ans. Amines containing replaceable hydrogen atom react with acid chloride or acid anhydride to form substituted amides. This reaction is called acylation reaction. In case of tertiary amines, there is no replaceable H atom and therefore these do not react with acetyl chloride or acetic anhydride and hence do not undergo acylation.

Q.14. Arrange the following sets in order of their basic strength in aqueous solution

(i) NH_3 , $\text{C}_6\text{H}_5\text{NH}_2$, CH_3NH_2 , $(\text{CH}_3)_3\text{N}$, $(\text{CH}_3)_2\text{NH}$

(Kerala S.B. 2018)

(ii) Aniline, *p*-nitroaniline, *p*-methylaniline.

(Hr. S.B. 2018, A.I.S.B. 2015)

Ans. (i) $\text{C}_6\text{H}_5\text{NH}_2 < \text{NH}_3 < \text{CH}_3\text{NH}_2 < \text{CH}_3\text{NH}_2 < (\text{CH}_3)_3\text{N}$

< *p*-nitroaniline < aniline < *p*-methylaniline

Q.15. Account for the following order of increasing basicity:



Ans. In $\text{RC}\equiv\text{N}$ the N atom is sp hybridised. In $\text{R}'\text{CH}=\text{NR}$ the N atom is sp^2 hybridised while in RNH_2 the N atom is sp^3 hybridised. The more s -character in the hybrid orbital of N with the lone pair of electrons, greater will be its tendency to be strongly held by the nucleus. Therefore, it will have lesser tendency to donate its electron pair and hence will behave as weak base. Thus, as s -character decreases from RCN to $\text{R}'\text{CH}=\text{NR}$ to RNH_2 , its basic character increases.

Q.16. Why do amines react as nucleophiles?

(A.I.S.B. 2007)

Ans. Amines have a lone pair of electrons on N atom and therefore, react as nucleophiles.

Q.17. Aniline does not undergo Friedel Crafts alkylation. Explain.

(Pb. S.B. 2013, Hr. S.B. 2015)

Ans. Aniline does not undergo Friedel-Craft alkylation reaction because of the formation of salt with aluminum chloride Lewis acid which is used as a catalyst. Due to this nitrogen of aniline acquires positive charge and hence acts as a strong deactivating group for further reaction.



Q.18. Although $-\text{NH}_2$ group is an ortho and para directing group, nitration of aniline gives along with ortho and para derivatives, meta derivative also.

(C.B.S.E. Sample Paper 2007)

Ans. Under strong acidic conditions of nitration, most of the aniline is converted into anilinium ion having NH_3^+ group. This group is a *m*-directing group, therefore, *m*-nitro aniline is also obtained along with *o*- and *p*-products.

Q.19. The presence of a base is needed in the ammonolysis of alkyl halides.

(C.B.S.E. Sample Paper 2007)

Ans. The ammonolysis of alkyl halides gives quaternary ammonium salt. The free amine can be obtained from ammonium salt by using a strong base.



Q.20. Aromatic primary amines cannot be prepared by Gabriel phthalimide synthesis.

(C.B.S.E. Sample Paper 2007)

Ans. Aromatic amines cannot be prepared by Gabriel phthalimide synthesis because aryl halides do not undergo nucleophilic substitution with the anion formed by phthalimide.

Q.21. Suggest a structural formula of a compound having molecular formula $\text{C}_6\text{H}_{11}\text{N}$ (A, which is optically active, dissolves in dil. aqueous HCl and release N_2 with nitrous acid).

Ans. $\text{C}_6\text{H}_5\text{CHCH}_3$



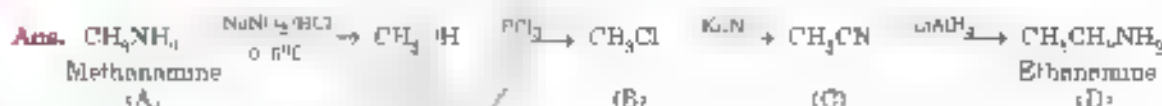
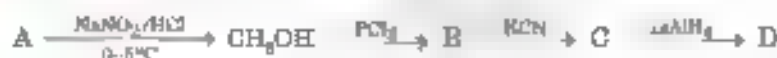
Q.22. Arrange the following in the increasing order of boiling points $\text{C}_2\text{H}_5\text{NH}_2$, $\text{C}_2\text{H}_5\text{OH}$, $(\text{CH}_3)_3\text{N}$

(D.S.B. 2015, A.I.S.B. 2015)

Ans. $(\text{CH}_3)_3\text{N} < \text{C}_2\text{H}_5\text{NH}_2 < \text{C}_2\text{H}_5\text{OH}$

Q.23. Identify A, B, C and D in the following conversions:

(Assam S.B. 2016)



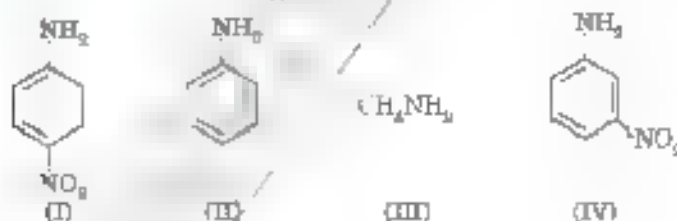
Methanamine
(A)

(B)

(C)

Ethanamine
(D)

Q.24. Arrange the following compounds in the decreasing order of basicity:



(W.B.S.B. 2016)

Ans. III > II > IV > I

Q.25. Name the following reactions:



(Assam S.B. 2017)

Ans. (i) Sandmeyer reaction (ii) Gattermann reaction

Q.26. Arrange the following in the increasing order of their pK_b values.

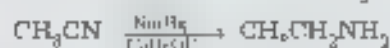


(A.I.S.B. 2018)

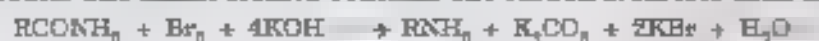
Ans. $\text{C}_6\text{H}_5\text{NH}_2 < \text{C}_6\text{H}_5\text{NHCH}_2\text{CH}_3 < \text{C}_6\text{H}_5\text{NHCH}_3$

Key Terms and Name Reactions

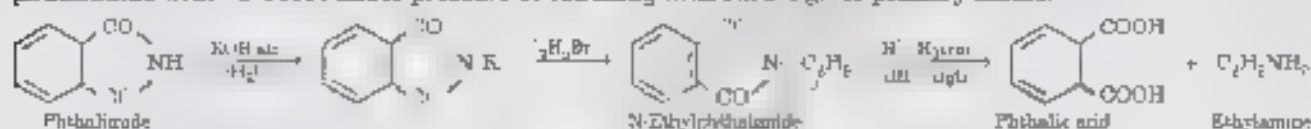
- ◆ **Exhaustive alkylation.** The process of converting an amine 1° or 2° or 3° into its quaternary ammonium salt on treatment with excess alkyl halide.
- ◆ **Deamination.** The process involving diazotisation of an amine followed by reduction of diazonium ester replacement of diazo group by hydrogen.
- ◆ **Mendius reaction.** The reduction of cyanide with sodium and alcohol.



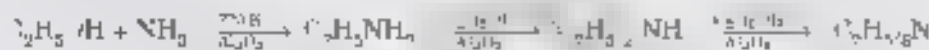
- ◆ **Hoffmann bromamide degradation.** Primary amides can be prepared from amides by treatment with Br_2 and KOH solution. The amine formed contains one carbon atom less than the parent amide.



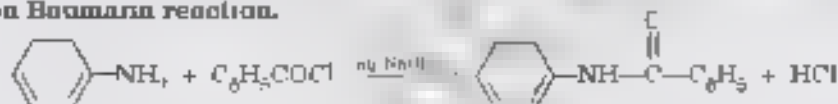
- ◆ **Gabriel phthalimide synthesis.** Phthalimide is treated with NaOH to give potassium phthalimide, which is treated with alkyl halide or benzyl halide to form N-alkyl or aryl phthalimide. The hydrolysis of N-alkyl phthalimide with 10% HCl under pressure or refluxing with NaOH gives primary amine.



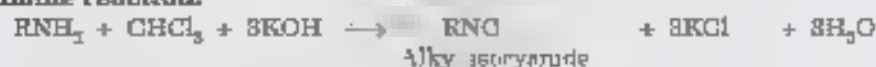
- ◆ **Sabatier and Mauje method.**



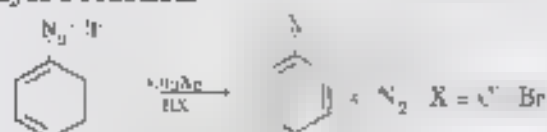
- ◆ **Schotten Baumann reaction.**



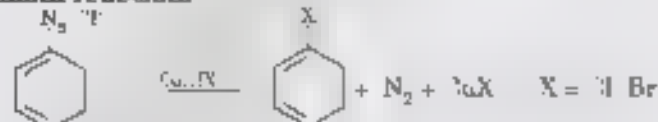
- ◆ **Carbonylamine reaction.**



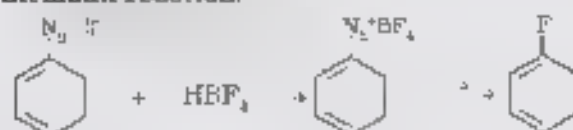
- ◆ **Sandmeyer's reaction.**



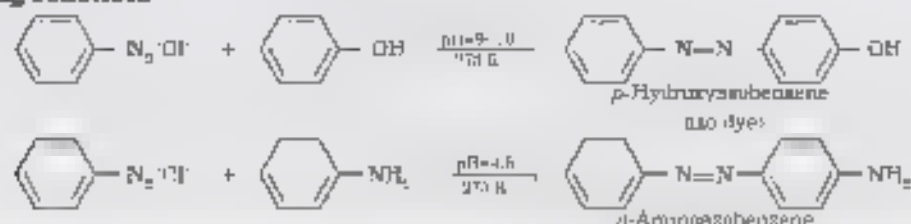
- ◆ **Gattermann reaction.**



- ◆ **Balz-Schiemann reaction.**



- ◆ **Coupling reaction.**



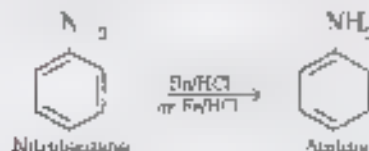
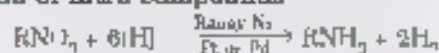
QUICK CHAPTER ROUND UP

Preparation of amines

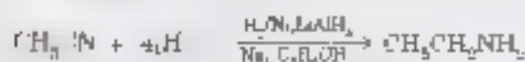
- By ammonolysis of alkyl halides



- Reduction of nitro compounds

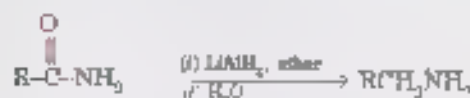


- Reduction of cyanides



⇒ Reaction of cyanides with Na, C_2H_5OH is **Mendius reaction**.

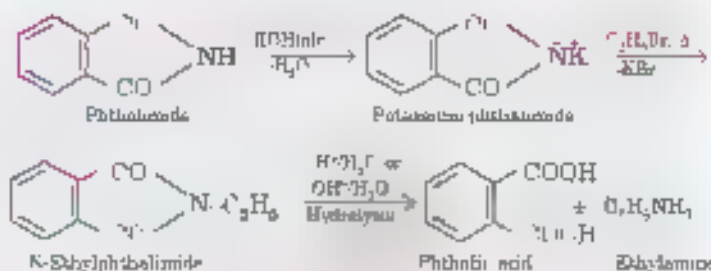
- Reduction of amides



- Hoffmann bromamide degradation

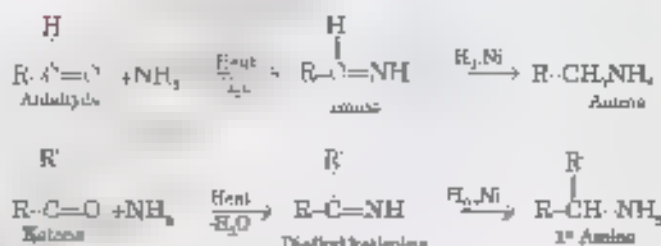


- Gabriel Phthalimide Synthesis

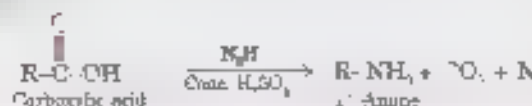


Aryl halides cannot be converted to aryl amines by **Gabriel synthesis**.

- Reductive amination of aldehydes and ketones



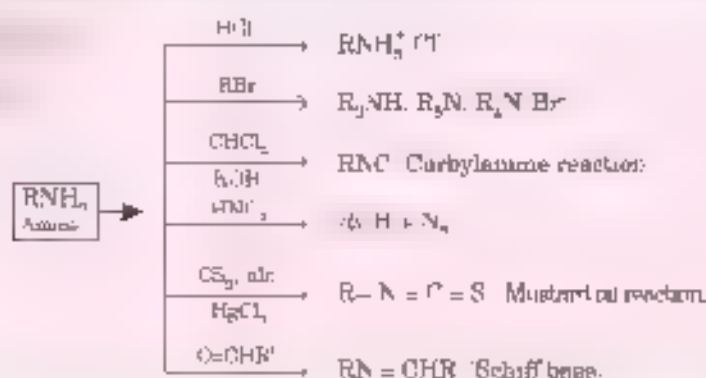
- Schmidt reaction



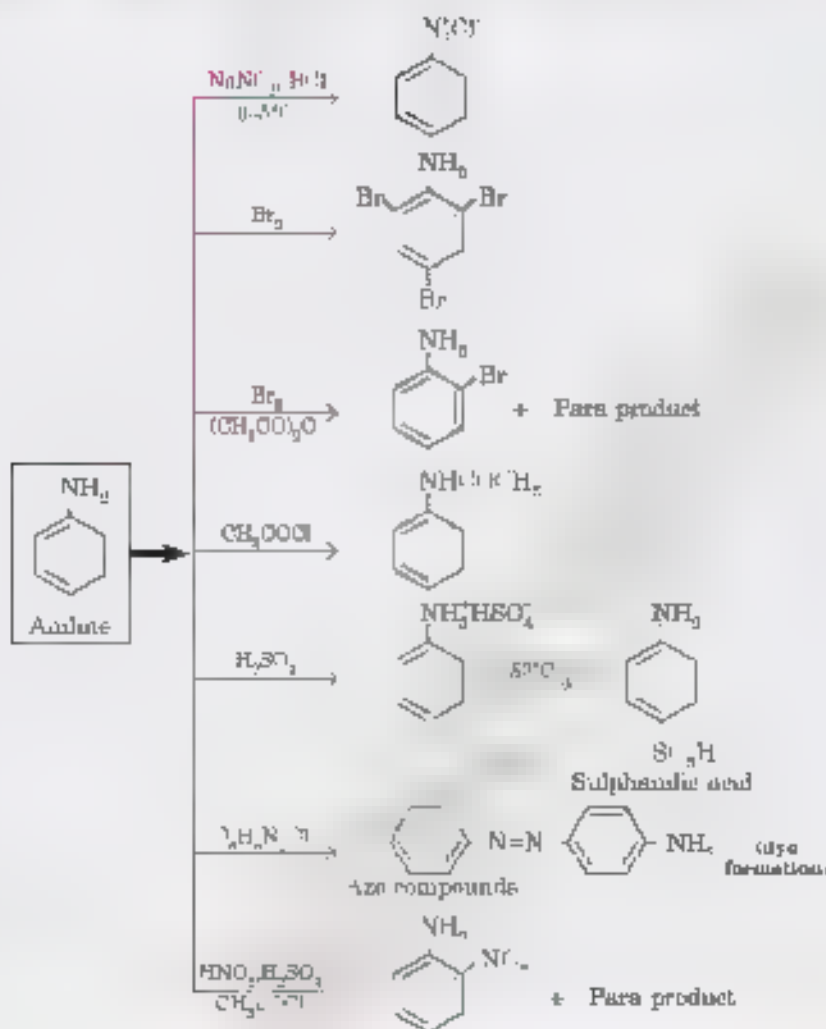
Properties of amines

- Because of the presence of a lone pair of electrons on the nitrogen atom of NH_2 group amines behave as **Lewis bases**.
- All aliphatic amines are more basic than ammonia. In aqueous solution the order of basic character is $(CH_3)_3NH^+ > CH_3NH_2 > (CH_3)_2NH$.
- Aniline is less basic than ethylamine.

Reactions of Amines



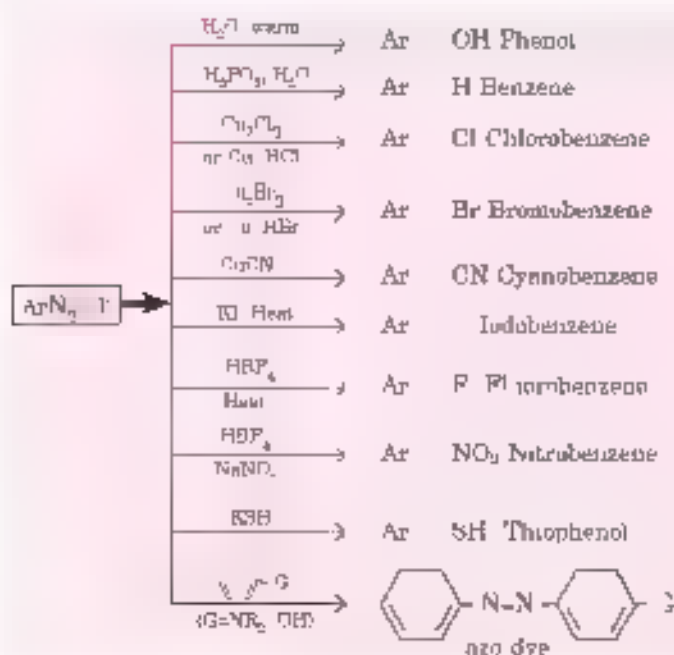
Reactions of Aniline



DIAZONIUM SALTS

Aromatic primary amines react with nitrous acid at 273–298 K (ice bath temperature), the product obtained is called diazonium salt $\text{C}_6\text{H}_5\text{N}_2^+\text{X}^-$. It contains the diazonium ion group $\text{N}\equiv\text{N}^+$ attached to aryl group.

- Aryl diazonium salts are more stable than alkyl diazonium salts.





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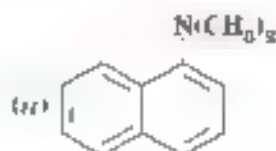
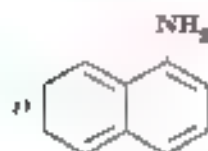
Solved



NCERT

In-text Questions

Q.1. Classify the following amines as primary, secondary and tertiary



Ans. Primary (1°)

ii Tertiary (3°)

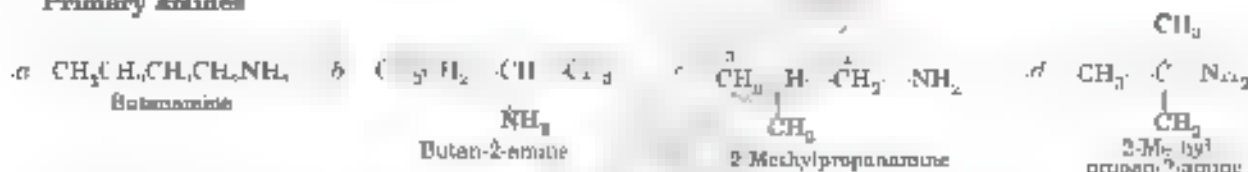
iii Primary (1°)

iv Secondary (2°)

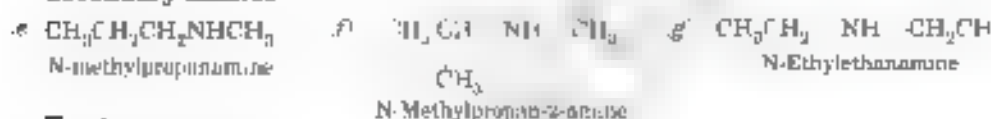
Q.2. (i) Write structures of different isomeric amines corresponding to the molecular formula, $C_4H_{11}N$.
 (ii) Write IUPAC names of all the isomers.
 (iii) What type of isomerism is exhibited by different pairs of amines?

Ans. (i), (ii)

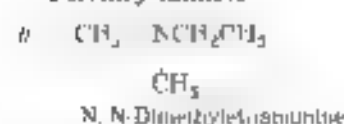
Primary amines



Secondary amines



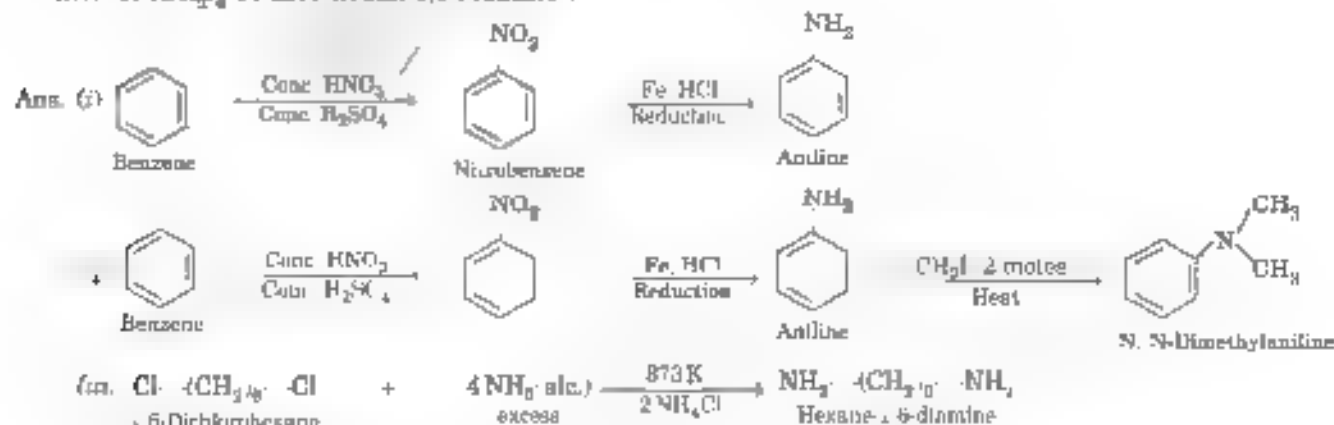
Tertiary amines



- (iii) (a) b and (e) (f) are position isomers.
 (c) (d), (b) (d) and (a) (d) are chain isomers.
 (e) (g) and (f) and (g) are metamers.

Q.3. How will you convert

- (i) Benzene into aniline?
 (ii) Benzene into N,N-dimethylaniline
 (iii) $Cl-(CH_2)_6-Cl$ into hexan-1,6-diamine?



Q.4. Arrange the following in increasing order of their basic strength

- (i) $C_2H_5NH_2$, $C_6H_5NH_2$, NH_3 , $C_8H_5CH_2NH_2$ and $(C_6H_5)_2NH$ (ii) $C_6H_5NH_2$, $(C_7H_7)_2NH$, $(C_7H_7)_2N$, $C_6H_5NH_2$
(iii) CH_3NH_2 , $(CH_3)_2NH$, $(CH_3)_3N$, $C_6H_5NH_2$, $C_6H_5CH_2NH_2$

Ans. (i) $C_6H_5NH_2 > C_6H_5NHCH_3 > C_6H_5CH_2NH_2 > C_6H_5NHCH_2CH_3 > NH_3$

Due to +I effect of the two $^+CH_3$ -groups in $C_6H_5C(CH_3)_2NH_2$ as compared to one in $C_6H_5NH_2$, the lone pair on N is more available in $C_6H_5C(CH_3)_2NH_2$ than $C_6H_5NH_2$ and therefore $C_6H_5C(CH_3)_2NH_2$ is more basic than $C_6H_5NH_2$. Now aromatic amine $C_6H_5NH_2$ is less basic than both $C_6H_5CH_2NH_2$ and $C_6H_5NHCH_3$ due to -I effect of C_6H_5 -group. Due to the presence of $^+CH_3$ -group, the electron density on the N atom becomes over and hence less basic. Comparing $C_6H_5NH_2$ and $C_6H_5CH_2NH_2$, N is directly bonded to the benzene ring and hence the lone pair of electrons on the N atom is delocalised over the benzene ring. In contrast, N in $C_6H_5CH_2NH_2$ is not directly bonded to the benzene ring and hence its lone pair is not delocalised over the benzene ring. Therefore, the lone pair of electrons on N atom in $C_6H_5CH_2NH_2$ is more easily available for protonation than that on the N atom in $C_6H_5NH_2$. Hence $C_6H_5CH_2NH_2$ is more basic than $C_6H_5NH_2$. Hence the correct order of basic character

11. Due to increase in +I inductive effect of C_6H_5 group, the electron density in N-atom increases and therefore the basic character is expected to increase as $C_6H_5NH_2 < (C_6H_5)_2NH < (C_6H_5)_3N$. In $C_6H_5NH_2$, the electron density on the N-atom decreases due to the delocalisation of the lone pair of electrons over the benzene ring. Therefore, all the three ethyl amines are more basic than $C_6H_5NH_2$. Though $C_2H_5NH_2$ is expected to be more basic than $C_2H_5CH_2NH_2$, it is less basic because of steric hindrance to H-bonding for solvation of conjugate acid derived from $C_2H_5CH_2NH_2$. Therefore, $C_2H_5CH_2NH_2$ is less basic than $C_2H_5NH_2$ but more basic than C_2H_5NH . So, the correct order of basic strength is



As explained in answer $\text{C}_6\text{H}_5\text{NH}_2$ is less basic than $\text{C}_6\text{H}_5\text{CH}_2\text{NH}_2$ and all methyl amines are more basic than these amines due to +I effect of $-\text{H}_3$ group. answer : ii) However $(\text{CH}_3)_3\text{N}$ is less basic than $\text{C}_6\text{H}_5\text{NH}_2$ and CH_3NH_2 due to steric hindrance and less stabilisation by H-bonding. Therefore the correct order is



6.5. Complete the following acid-base reactions and name the products:

- $$n, (H_2I)H_2(H_2NH_2 + HCl) \quad + \quad (b) \quad C_{10}H_{17}N + HCl$$

Ann. (\equiv $\text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2$ + HCl) + $\text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_3^+\text{Cl}^-$
 n-propylamine n-propylammonium chloride

$$b \quad (C_2H_5)_3N + HCl \rightarrow (C_2H_5)_3NH^+Cl^-$$

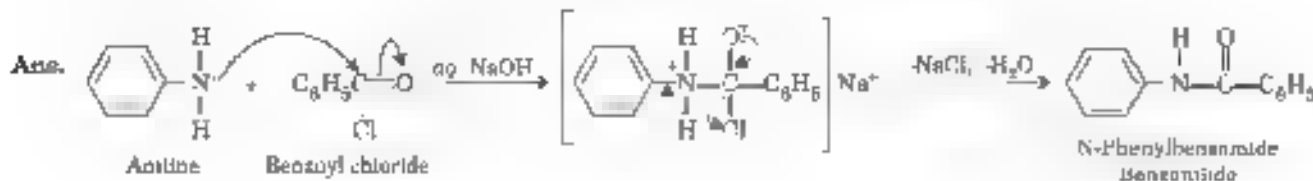
Triethylammonium chloride

Q.6. Write reactions of the final alkylation product of aniline with excess of methyl iodide in the presence of sodium carbonate solution.

Ans.

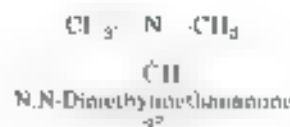
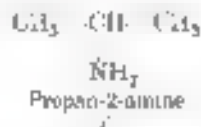
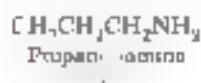
$$\begin{array}{l}
 \text{C}_6\text{H}_5\text{NH}_2 + \text{CH}_3\text{I} \xrightarrow{\text{Aniline}} \text{C}_6\text{H}_5\text{NH}_2^+\text{CH}_3\text{I}^- \text{N-Methylanilinium iodide} \\
 2[\text{C}_6\text{H}_5\text{NH}_2\text{CH}_3\text{I} + \text{Na}_2\text{CO}_3] \longrightarrow 2\text{C}_6\text{H}_5\text{NHCH}_3 + \text{CO}_2 + 2\text{NaI} \\
 \text{N-Methylaniline} \\
 \text{C}_6\text{H}_5\text{NHCH}_3 \xrightarrow[\text{Na}_2\text{CO}_3]{\text{CH}_3\text{I}} \text{C}_6\text{H}_5\text{N}(\text{CH}_3)_2 + \text{CO}_2 + 2\text{NaI} \\
 \text{N,N-Dimethyl aniline} \\
 \text{C}_6\text{H}_5\text{N}(\text{CH}_3)_2 + \text{CH}_3\text{I} \longrightarrow \text{C}_6\text{H}_5\text{N}^+(\text{CH}_3)_3\text{I}^- \\
 \text{N,N,N-Trimethylanilinium iodide} \\
 2\text{C}_6\text{H}_5\text{N}^+(\text{CH}_3)_3\text{I}^- + \text{Na}_2\text{CO}_3 \longrightarrow [\text{C}_6\text{H}_5\text{N}^+(\text{CH}_3)_3\text{CO}_3]^{2-} + 2\text{NaI} \\
 \text{N,N,N-Trimethylanilinium carbonate}
 \end{array}$$

Q.7. Write chemical reaction of aniline with benzoyl chloride and write name of the product obtained.

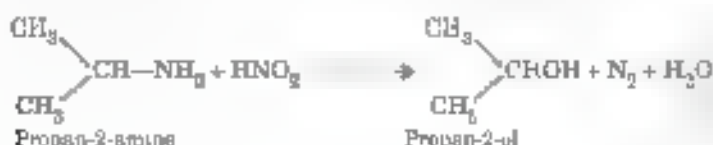


Q.8. Write structures of different isomers corresponding to the molecular formula, C_3H_9N . Write IUPAC names of the isomers which will liberate nitrogen gas on treatment with nitrous acid.

Ans. Four structural isomers are possible



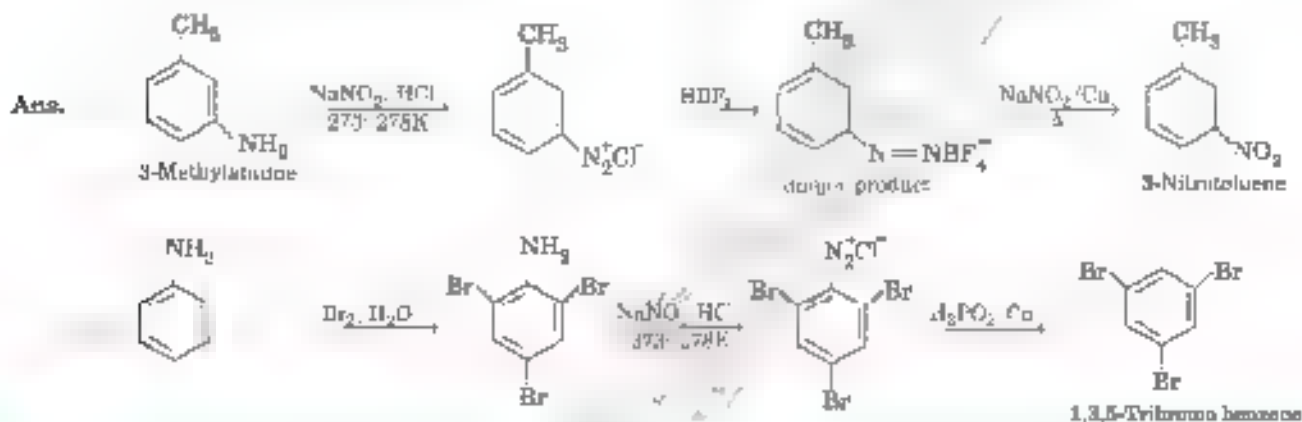
Only 1° amines react with HNO_2 to liberate N_2 gas



Q.9. Convert

(i) 3-Methylaniline into 3-nitrotoluene

(ii) Aniline into 1,3,5-tribromobenzene.



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Textbook Exercises

Q.1. Write IUPAC names of the following compounds and classify them into primary, secondary and tertiary amines.

- (i) $CH_3CH_2CH_2NH_2$ (ii) $CH_3CH_2CH_2NHCH_3$ (iii) $(CH_3)_2NCH_2CH_2CH_3$ (iv) $(CH_3)_3CNH_2$
 (v) $C_6H_5NHCH_3$ (vi) $(CH_3CH_2)_3NCH_3$ (vii) $m\text{-BrC}_6H_4NH_2$

- Ans.** (i) Propan-1-amine (1°) (ii) N-Methylpropan-1-amine (1°) (iii) N-Ethyl-N-methylethanamine (3°)
 (iv) N-Methylpropan-2-amine (2°) (v) N-Methylbenzenamine or N-Methylaniline
 (vi) 3-Bromobenzenamine or 3-Bromoaniline (1°)

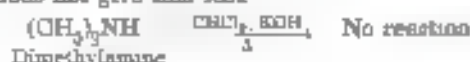
Q.2. Give one chemical test to distinguish between the following pairs of compounds.

- (i) Methylamine and dimethylamine (ii) Secondary and tertiary amines
 (iii) Ethylamine and aniline (iv) Aniline and benzylamine
 (v) Aniline and N-methylaniline

Ans. These can be distinguished by carbylamine test. When heated with alcoholic solution of KOH and chloroform, methylamine gives foul smell of methyl isocyanide.



Dimethylamine does not give this test.



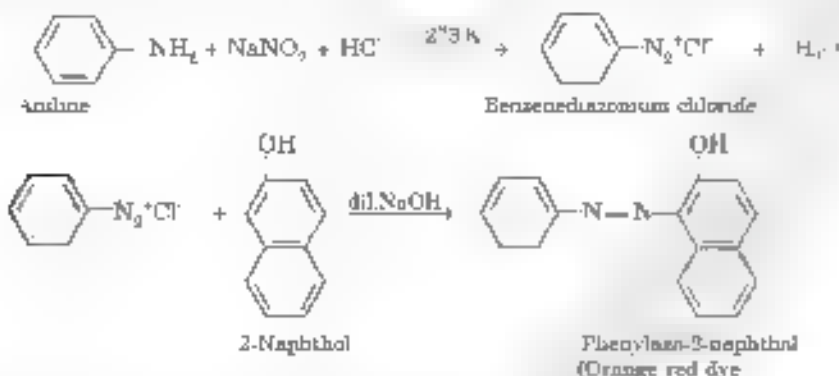
- Secondary amines give Libermann nitrosoamine test while 2° amines do not. 2° amine on treatment with HNO_2 prepared in situ by the action of H^+ on NaNO_2 gives yellow coloured oily N-nitrosoamine.



N-Nitrosodiethylamine on warming with a crystal of phenol and conc. H_2SO_4 gives a green solution which when made alkaline with aqueous NaOH turns deep blue and then red on dilution. Tertiary amines do not give this test.

- (iv) These can be distinguished by azo dye test.

Dissolve the compound in conc. HCl and add ice-cold solution of HNO_2 , NaNO_2 + dil. HCl and then treat it with an alkaline solution of 2-naphthol. Appearance of brilliant orange or red dye indicates aniline.



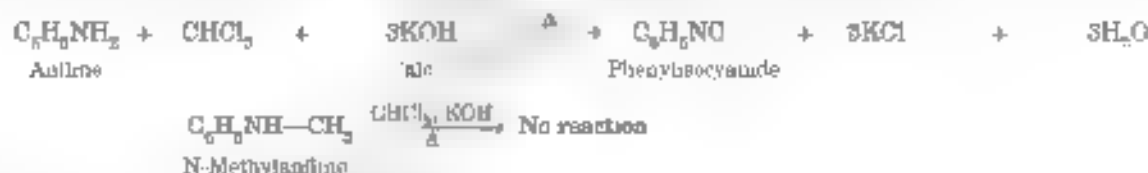
Ethylamine does not form dye. It will give brick aftertaste due to the evolution of N_2 but solution remains clear.

- (v) These can be distinguished by azo dye test.

Aniline reacts with HNO_2 , NaNO_2 + dil. HCl at $273-278\text{K}$ to form stable benzene diazonium chloride which on treatment with an alkaline solution of 2-naphthol gives an orange dye as given in reaction (iv).

Benzylamine does not give azo dye test.

- (vi) These can be distinguished by carbylamine test. Aniline being primary amine gives carbylamine test, i.e. when heated with an alcoholic solution of KOH and CHCl_3 it gives foul smell of phenyl isocyanide.

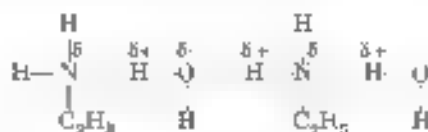


Q.3. Account for the following :

- pK_a of aniline is more than that of methylamine. (D.S.B. 2008)
- Ethylamine is soluble in water, whereas aniline is not.
- Methylamine in water reacts with ferric chloride to precipitate hydrated ferric oxide.
- Although amino group is π - and ρ -directing in aromatic electrophilic substitution reactions, aniline on nitration gives a substantial amount of m -nitroaniline.
- Aniline does not undergo Friedel Crafts reaction. (D.S.B. 2008)
- Diazonium salts of aromatic amines are more stable than those of aliphatic amines.
- Gabriel phthalimide synthesis is preferred for synthesising primary amines.

Ans. In aniline, the lone pair of electrons on N atom is delocalized over the benzene ring. As a result, electron density on the nitrogen decreases. On the other hand, in CH_3NH_2 , the effect of CH_3 group increases the electron density on N atom. Therefore, aniline is less basic than methylamine and hence pK_b of aniline is higher than that of methylamine.

• Ethylamine dissolves in water due to intermolecular hydrogen bonding as shown below.

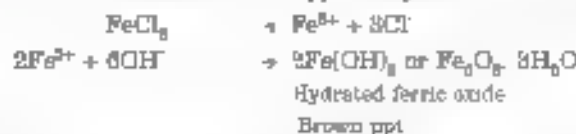


However, because of large hydrophobic part i.e. hydrocarbon part of aniline, the extent of hydrogen bonding is less and therefore, aniline is insoluble in water.

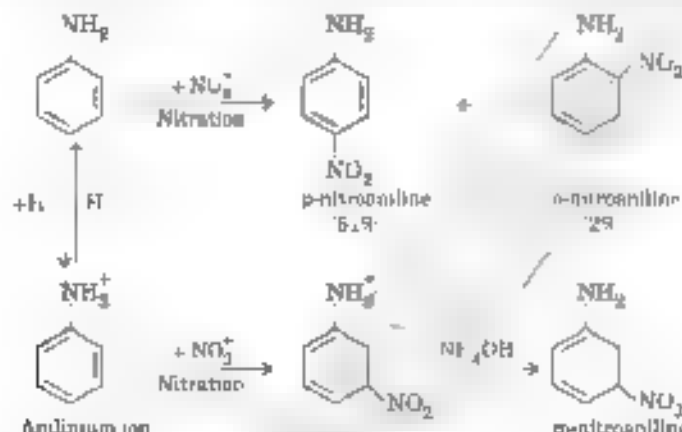
- c. Methylamine is more basic than water and therefore, accepts a proton from water forming OH^- ions.



These OH^- ions combine with Fe^{3+} ions to form brown ppt. of hydrated ferric oxide



- d. Under **strongly** acidic conditions of nitration (in the presence of a mixture of conc. HNO_3 + H_2SO_4) aniline gets protonated and is converted into anilinium ion having NH_3^+ group. This group is deactivating group and is π -directing. So the nitration of aniline gives *o*, *p*-nitroaniline mainly *p*-product while the nitration of 'unammoniated' anion gives *o*-nitroaniline.



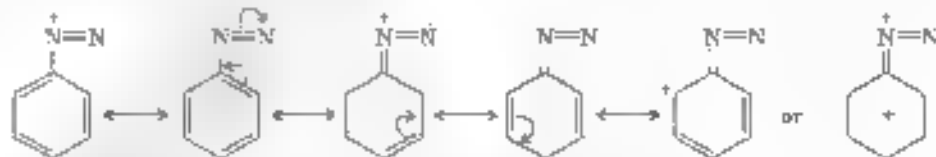
Thus, nitration of aniline gives a substantial amount of *o*-nitroaniline due to protonation of aniline.

- (v) Anilines being a Lewis base reacts with Lewis acid such as AlCl_3 to form a salt



As a result N of aniline acquires +ve charge and hence + acts as a strong deactivating group for electrophilic substitution reaction. Hence aniline does not undergo Friedel Crafts reaction.

- (vi) The diazonium salts of aromatic amines are more stable than those of aliphatic amines because of dispersal of positive charge on the benzene ring due to resonance



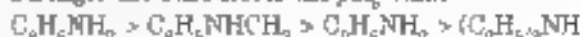
This type of resonance stability is not possible in alkyl diazonium salts

- (vii) Inbaur's phenylhydrazide reaction gives pure 1° amines without any impurity of 2° or 3° amines. Therefore it is preferred for the synthesis of 1° amines.

Q.4. Arrange the following :

- In decreasing order of the pK_b values : $\text{C}_2\text{H}_5\text{NH}_2$, $\text{C}_6\text{H}_5\text{NHCH}_3$, $(\text{C}_2\text{H}_5)_2\text{NH}$ and $\text{C}_6\text{H}_5\text{NH}_2$ (D.S.B. 2010)
- In decreasing order of basic strength : $\text{C}_6\text{H}_5\text{NH}_2$, $\text{C}_6\text{H}_5\text{N}^+\text{CH}_3$, $(\text{C}_6\text{H}_5)_2\text{NH}$ and CH_3NH_2 (D.S.B. 2010)
- Increasing order of basic strength :
 - Aniline, *p*-nitroaniline and *p*-toluidine
 - $\text{C}_6\text{H}_5\text{NH}_2$, $\text{C}_6\text{H}_5\text{NHCH}_3$, $\text{C}_6\text{H}_5\text{CH}_2\text{NH}_2$ (D.S.B. 2010)
- Decreasing order of basic strength in gas phase : $\text{C}_2\text{H}_5\text{NH}_2$, $\text{C}_2\text{H}_5\text{NH}$, $\text{C}_2\text{H}_5\text{N}$ and NH_3
- Increasing order of boiling point : $\text{C}_2\text{H}_5\text{OH}$, $(\text{CH}_3)_2\text{NH}$, $\text{C}_2\text{H}_5\text{NH}_2$
- Increasing order of solubility in water : $\text{C}_6\text{H}_5\text{NH}_2$, $(\text{C}_2\text{H}_5)_2\text{NH}$, $\text{C}_2\text{H}_5\text{NH}_2$

Ans. (i) Stronger the base lesser the pK_b value.



Refer In-text Q.4



Refer Intext Q. 3



In gas phase reactions, the stabilization of the conjugate acids due to hydrogen bonding is absent.

- (i) Since the electronegativity of O is more than that of N, alcohols form stronger hydrogen bonds than amines. Therefore, the b.p. of C_2H_5OH (mol. mass = 46) is higher than those of $CH_3)_2NH$ and $C_2H_5NH_2$, each having mol. mass = 45. Further, since the extent of hydrogen bonding depends upon the number of H-atoms on N atom, therefore 1° amines with two H atoms on the N atom have higher b.p. than 2° amines of comparable molecular mass having only one H atom on N. Thus, the boiling point of $(C_2H_5)_2NH$ is more than that of $C_2H_5NH_2$. Thus, the b.p.s of given compounds increase as,

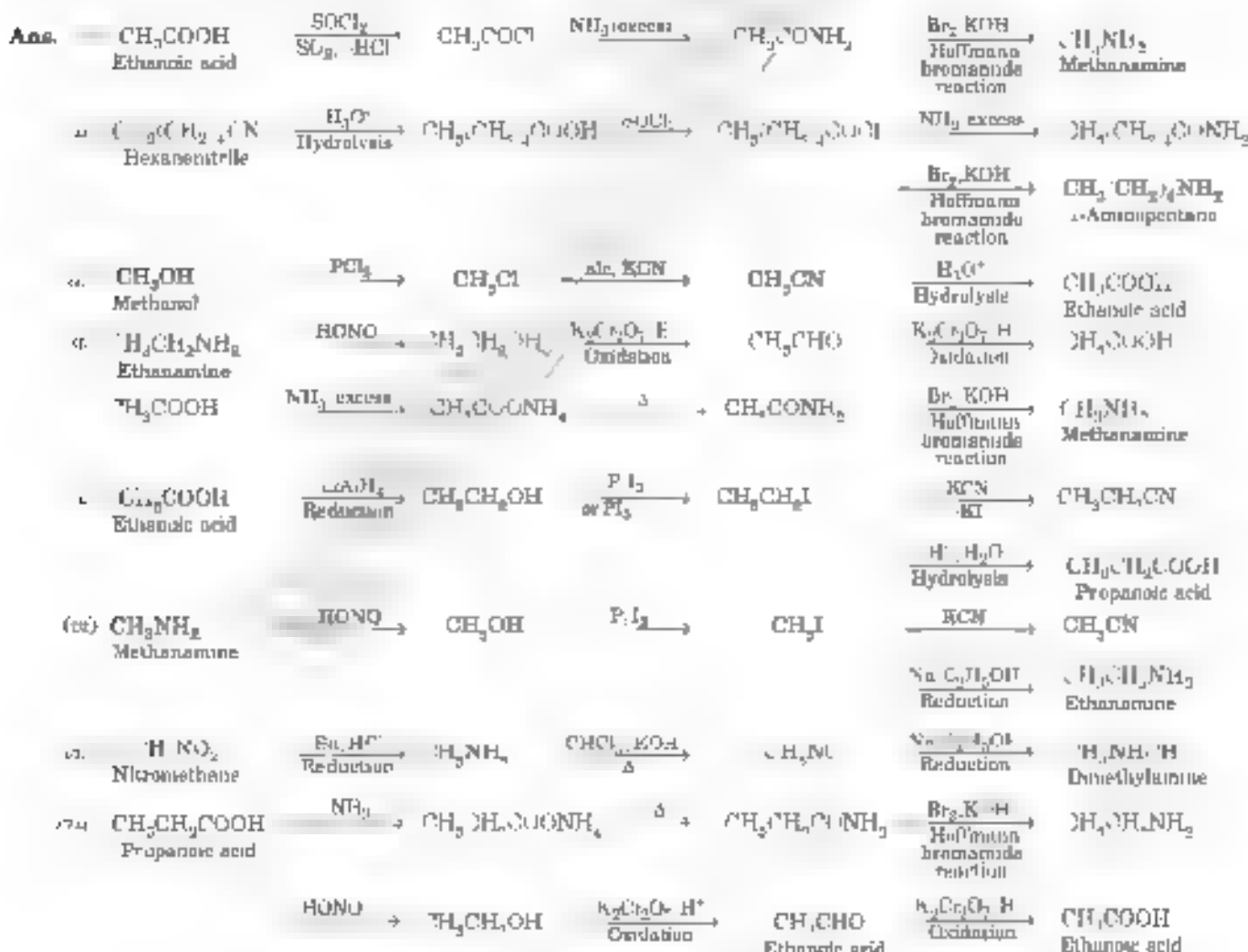


- (ii) Solubility decreases with increase in molecular mass of amines due to increase in size of the hydrophobic hydrocarbon part and with the decrease in the number of H atoms on the N-atom which form hydrogen bonds. Among the given compounds, $C_6H_5NH_2$ has higher molecular mass (93) followed by $(C_2H_5)_2NH$ (73) while $C_2H_5NH_2$ has lowest molecular mass of 45. Thus, the solubility increases in the order



Q.5. How will you convert

- (i) Ethanoic acid into methanamine
 (ii) Methanol to ethanoic acid
 (iii) Ethanoic acid into propanoic acid
 (iv) Nitromethane into dimethylamine
 (v) Hexanenitrile into 1-aminopentane
 (vi) Ethanamine into methanamine
 (vii) Methanamine into ethanamine
 (viii) Propanoic acid into ethanoic acid ?



Q.6. Describe the method for the identification of primary, secondary and tertiary amines. Also write chemical equations of the reactions involved.

Ans. Refer Page 28-29

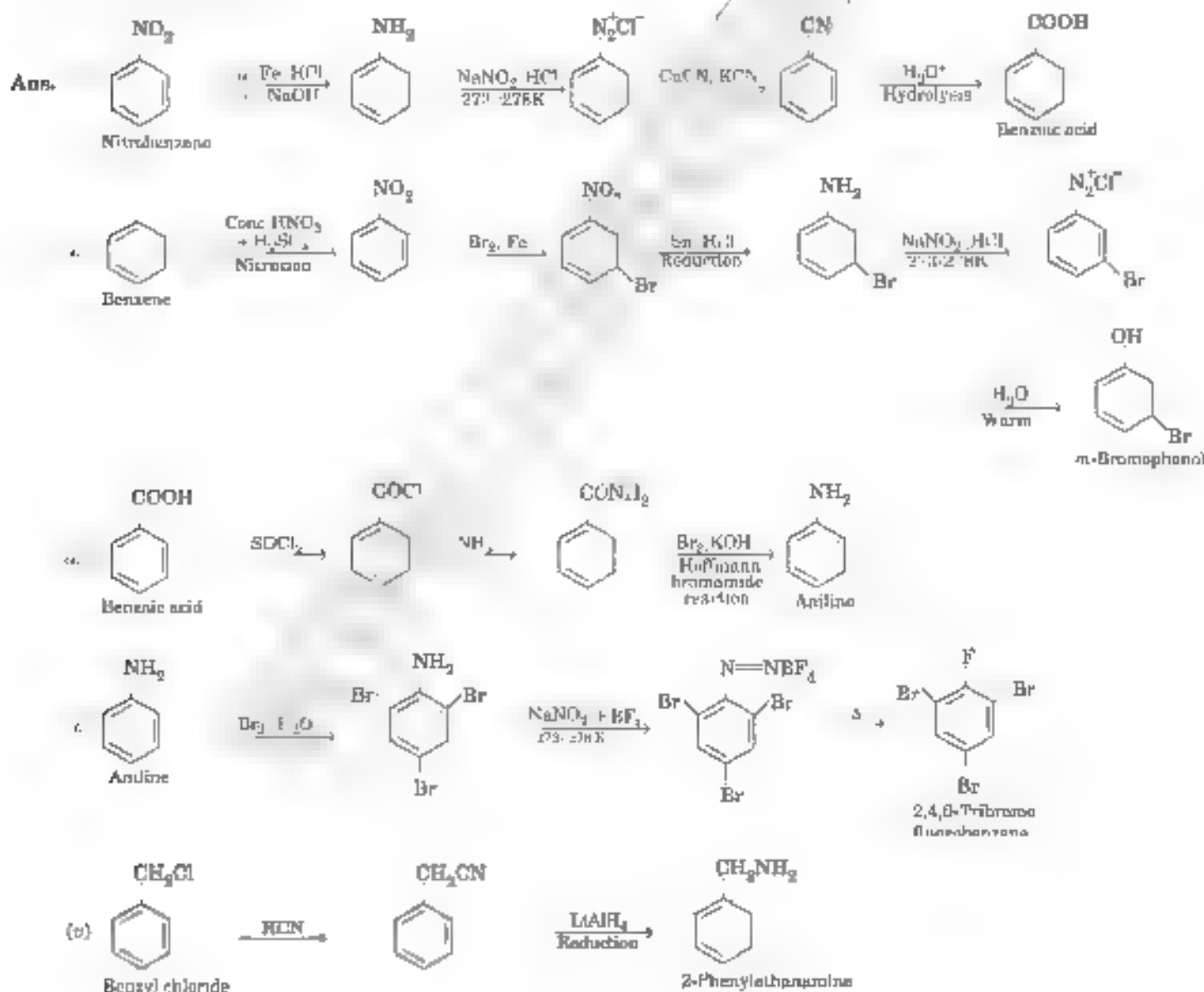
Q.7. Write short notes on the following

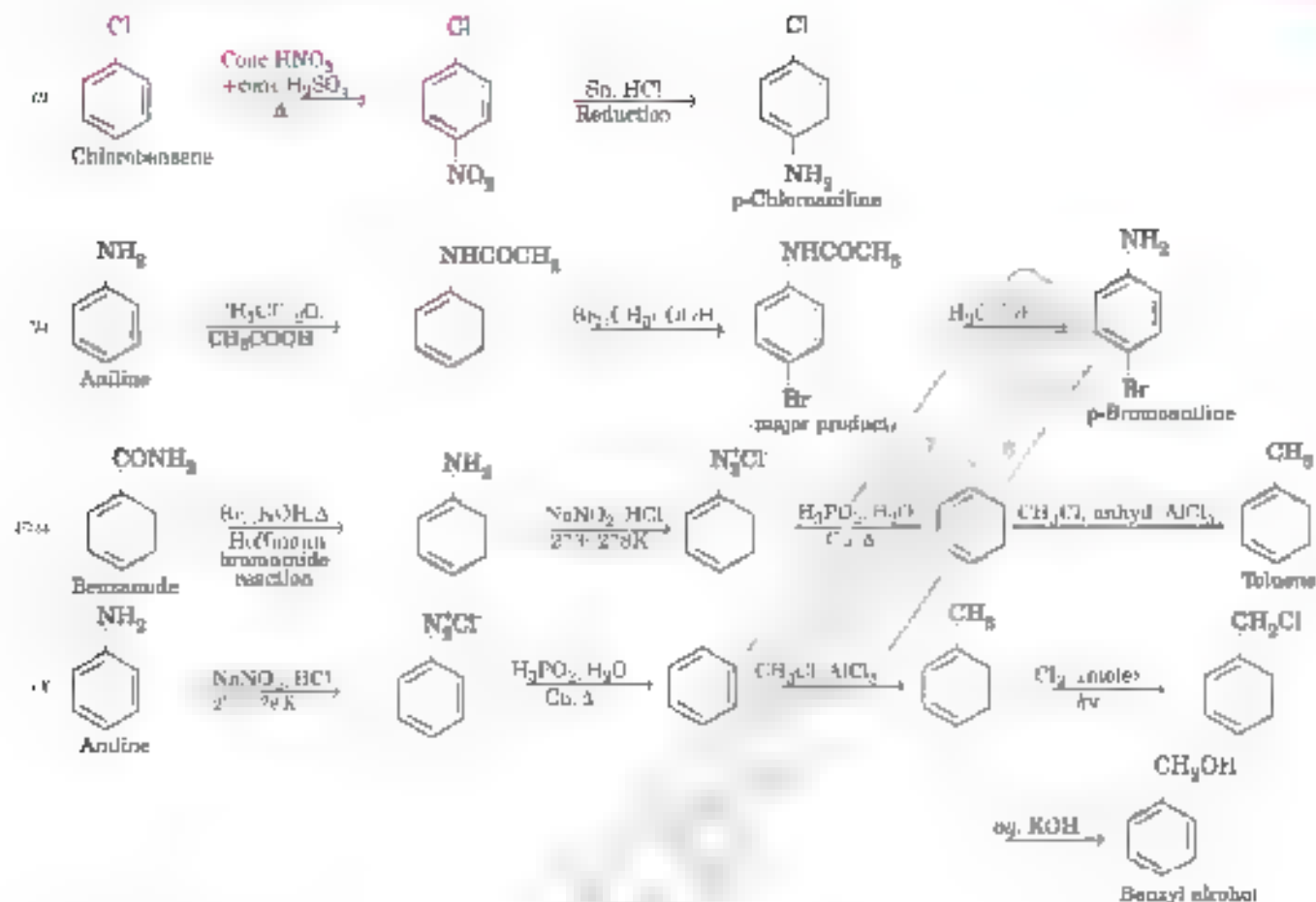
- | | |
|-------------------------------------|-------------------------|
| i) Carbylamine reaction | (ii) Diazotisation |
| ii) Hoffmann's bromamide reaction | (iii) Coupling reaction |
| (v) Ammonolysis | (vi) Acetylation |
| (vii) Gabriel phthalimide synthesis | |

Ans. Refer Text Page 28 & Page 41 & Page 39 reaction i & Page 40 & Page 39 & Page 29 or page 14

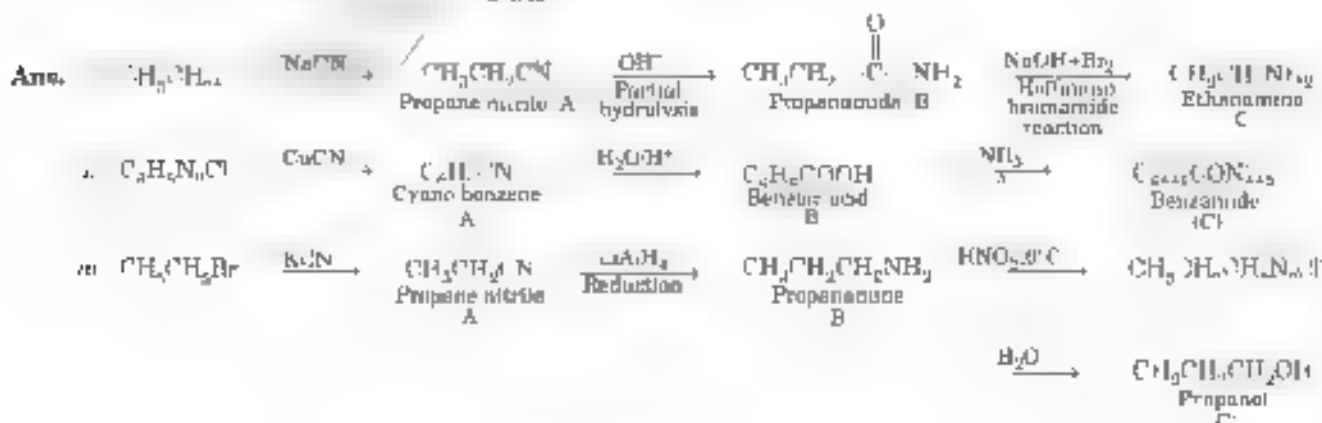
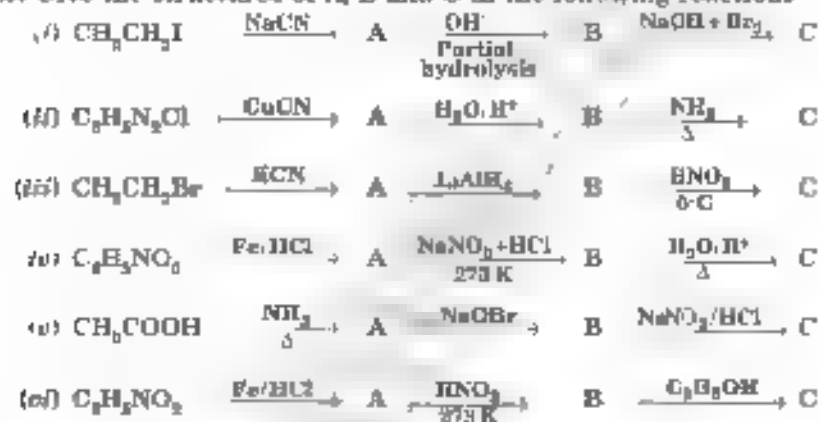
Q.8. Accomplish the following conversions.

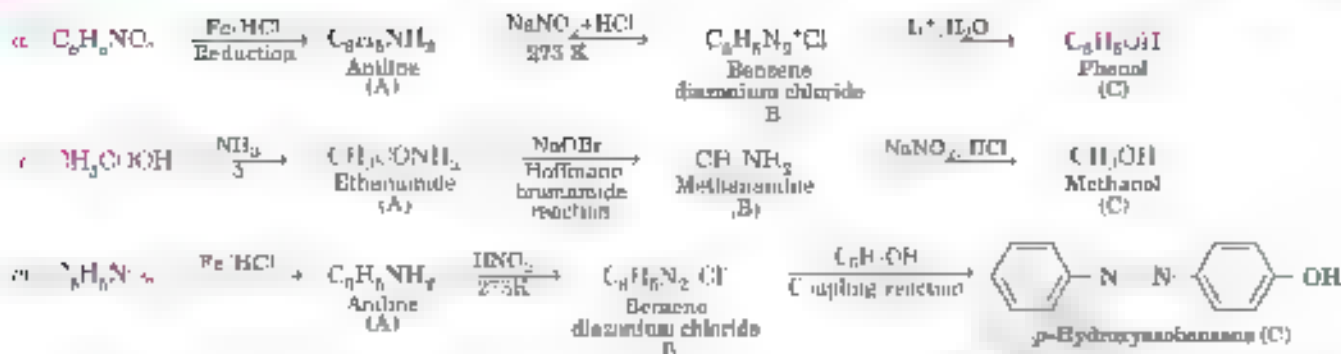
- | | |
|---|--|
| i) Nitrobenzene to benzoic acid | (ii) Benzene to <i>m</i> -bromophenol |
| ii) Benzoic acid to aniline | iv) Aniline to 2,4,6-tribromofluorobenzene |
| (v) Benzyl chloride to 2-phenylethanamine | vi) Chlorobenzene to <i>p</i> -chloroaniline |
| (vii) Aniline to <i>p</i> -bromoaniline | (viii) Benzamide to toluene |
| ix) Aniline to benzyl alcohol | |





Q.9. Give the structures of A, B and C in the following reactions





Q.10. An aromatic compound 'A' on treatment with aqueous ammonia and heating forms compound 'B' which on heating with Br_2 and KOH forms a compound 'C' of molecular formula $\text{C}_6\text{H}_7\text{N}$. Write the structures and IUPAC names of compounds A, B and C.

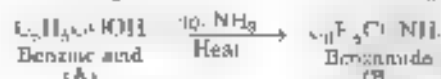
Ans. Since the compound 'C' of molecular formula $\text{C}_6\text{H}_7\text{N}$ is formed from B on treatment with Br_2 and KOH (Hoffmann bromamide reaction) therefore the compound 'B' must be an amide and 'C' must be an amine. The only aromatic amine having molecular formula $\text{C}_6\text{H}_7\text{N}$ is $\text{C}_6\text{H}_5\text{NH}_2$ (aniline).

• Since 'C' is amine, the amide from which is formed by must be benzamide ($\text{C}_6\text{H}_5\text{CONH}_2$).



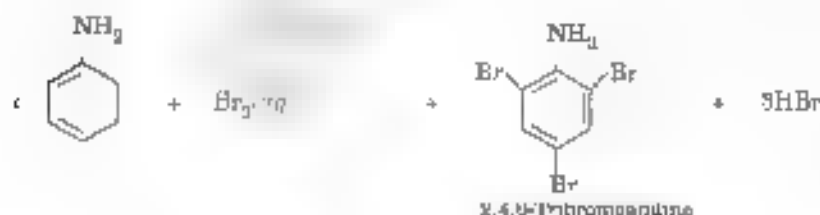
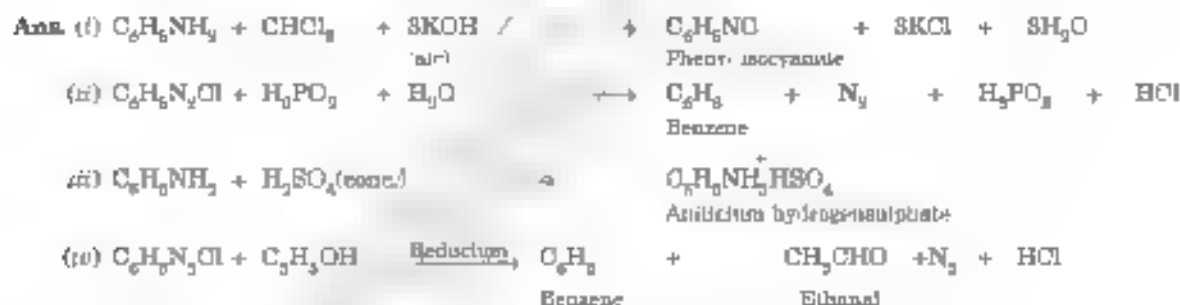
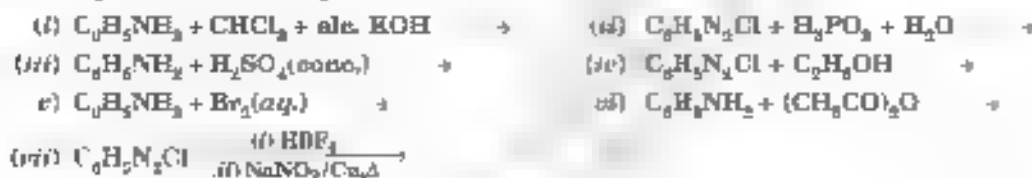
Thus, B is benzamide

• Since B is formed from A with aqueous ammonia and heating therefore compound A must be benzoic acid.



Thus, A = $\text{C}_6\text{H}_5\text{COOH}$, B = $\text{C}_6\text{H}_5\text{CONH}_2$, C = $\text{C}_6\text{H}_5\text{NH}_2$

Q.11. Complete the following reactions :



Q.12. Why aromatic primary amines cannot be prepared by Gabriel phthalimide synthesis ?

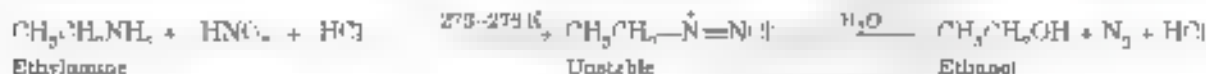
Ans. Refer Text (Page 14).

Q.13. How do aromatic and aliphatic primary amines react with nitrous acid ?

Ans. Aromatic primary amines react with HNO_2 at 273–278 K to form aromatic diazonium salts.



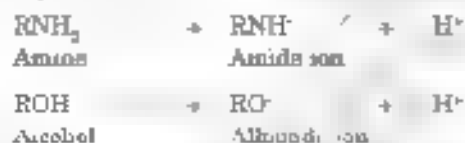
Aliphatic primary amines also react with HNO_2 at 273–278 K to form aliphatic diazonium salts. However, these are unstable even at low temperature and therefore, decompose readily to form alcohols, generally predominate and N_2 is evolved.



Q.14. Give plausible explanation for each of the following

- Why are amines less acidic than alcohols of comparable molecular masses ?
- Why are primary amines higher boiling than tertiary amines ?
- Why are aliphatic amines stronger bases than aromatic amines ?

Ans. Loss of proton from amines give amide ion whereas loss of a proton from alcohol gives an alkoxide ion



Since O is more electronegative than N, therefore, it can accommodate the -ve charge more easily than RNH⁻. Consequently RO⁻ is more stable than RNH⁻. Thus, alcohols are more acidic than amines.

Primary amines RNH_2 have two hydrogen atoms on the N atom and therefore, form intermolecular hydrogen bonding



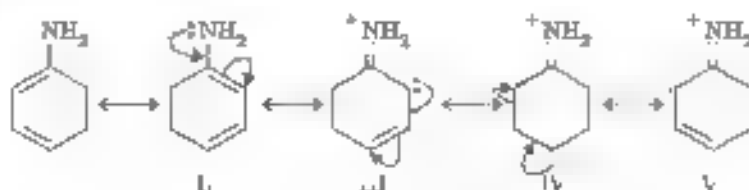
Tertiary amines R_3N do not have hydrogen atoms on the N atom and therefore, these do not form hydrogen bonds. As a result of hydrogen bonding in primary amines, they have higher boiling points than tertiary amines of comparable molecular mass. For example, b.p. of n-butylamine is 361 K while that of tert-butylamine is 310 K.

Both arylamines and alkylamines are basic in nature due to the presence of one pair on N-atom. But arylamines are less basic than alkylamines. For example, aniline is less basic than ethylamine as shown by K_b values.

Ethylamine $K_b = 4.7 \times 10^{-4}$

Aniline $K_b = 4.2 \times 10^{-10}$

The less basic character of aniline can be explained on the basis of aromatic ring present in aniline. Aniline can have the following resonating structures



It is clear from the above resonating structures that three of these (III, IV and V) acquire some positive charge on N atom. As a result, the pair of electrons become less available for protonation. Hence, aniline is less basic than ethyl amine in which there is no such resonance.



NCERT

Exemplar Problems

Subjective Questions

Remember

Objective Questions from Exemplar Problems are given in Competition File page 107

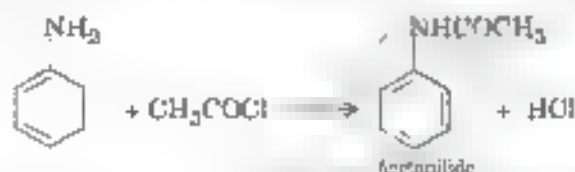
Short Answer Type Questions

Q.1 What is the role of HNO_3 in the nitrating mixture used for nitration of benzene?

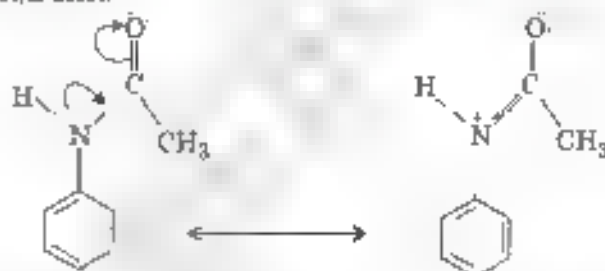
Ans. HNO_3 acts as a base in the nitrating mixture $\text{HNO}_3 + \text{H}_2\text{SO}_4$ and provides the electrophile $\text{HNO}_3 + \text{H}_2\text{SO}_4 \rightarrow \text{NO}_2^+ + \text{HSO}_4^- + \text{H}_2\text{O}$
Electrophile

Q.2 Why is NH_2 group of aniline acetylated before carrying out nitration?

Ans. Aniline is very reactive. The direct nitration of aniline is unsatisfactory because of the susceptibility of the ring towards oxidation with nitric acid. However, to carry out nitration, the activation of benzene ring is reduced by first acetylating aniline with acetyl chloride.



Explanation of reduced reactivity of NH_2 group in acetanilide. In acetanilide the oxygen of the group withdraws electrons from NH_2 group as shown below



As a result, the electron pair on nitrogen gets displaced to the carbonyl group. Therefore, the unshared pair of electrons on nitrogen is less available for donation to the aromatic ring. Consequently the electron density at ortho and para positions in the benzene ring gets reduced which in turn results in reduced reactivity towards electrophilic substitution of benzene.

Q.3 What is the product when $\text{C}_6\text{H}_5\text{CH}_2\text{NH}_2$ reacts with HNO_3 ?

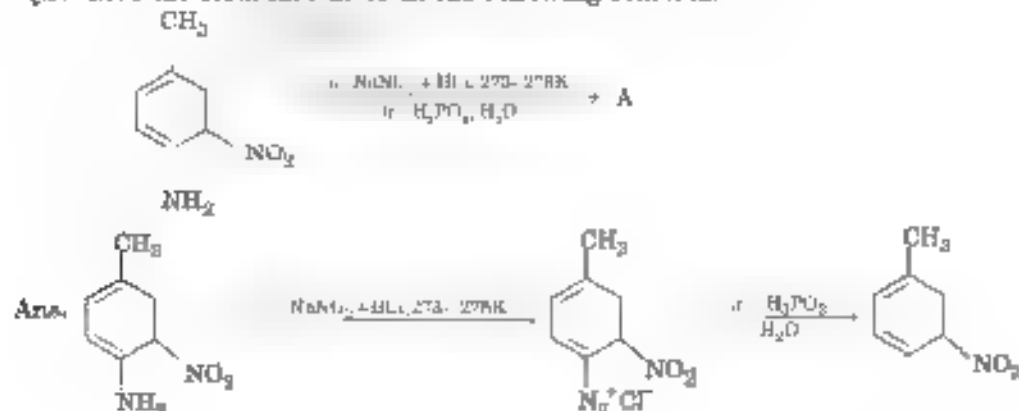
Ans. $\text{C}_6\text{H}_5\text{CH}_2\text{NH}_2 + \text{HONO} \rightarrow \text{C}_6\text{H}_5\text{CH}_2\text{OH} + \text{N}_2 + \text{H}_2\text{O}$

Q.4 What is the best reagent to convert nitrile to primary amine?

Ans. Reduction of nitriles with $\text{Na}/\text{alcohol}$ or LiAlH_4 gives primary amine



Q.5 Give the structure of 'A' in the following reaction.



Q.6. What is Hinsberg reagent?

Ans. Benzene sulphonylchloride $\text{C}_6\text{H}_5\text{SO}_2\text{Cl}$

Q.7. Why is benzene diazonium chloride not stored and is used immediately after its preparation?

Ans. Benzene diazonium chloride is very unstable and therefore, it is not stored.

Q.8. Why does acetylation of NH_2 group of aniline reduce its activating effect?

Ans. Refer Q. No. 2.

Q.9. Explain why MeNH_2 is stronger base than MeOH ?

Ans. Nitrogen is less electronegative than oxygen. Therefore, lone pair of electrons on nitrogen is readily available for donation. Hence, MeNH_2 is more basic than MeOH .

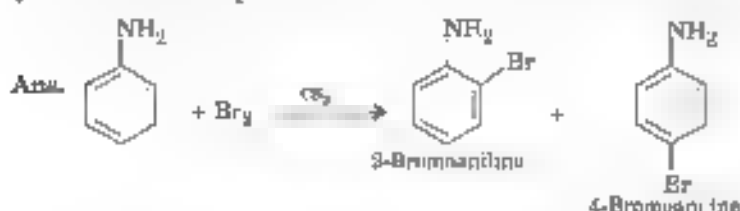
Q.10. What is the role of pyridine in the acylation reaction of amines?

Ans. Pyridine and other bases are used to remove the side product H^+ from the reaction mixture.

Q.11. Under what reaction conditions (acidic/basic), the coupling reaction of aryl diazonium chloride with aniline is carried out?

Ans. Coupling reaction is carried out in mild basic conditions.

Q.12. Predict the product of reaction of aniline with bromine in non-polar solvent such as CS_2 .



Q.13. Arrange the following compounds in increasing order of dipole moment.

$\text{CH}_3\text{CH}_2\text{CH}_3$, $\text{CH}_3\text{CH}_2\text{NH}_2$, $\text{CH}_3\text{CH}_2\text{OH}$

Ans. $\text{CH}_3\text{CH}_2\text{CH}_3 < \text{CH}_3\text{CH}_2\text{NH}_2 < \text{CH}_3\text{CH}_2\text{OH}$

Q.14. What is the structure and IUPAC name of the compound, allyl amine?

Ans. $\text{H}_2\text{C}=\text{CH}-\text{CH}_2\text{NH}_2$, Prop-2-en-1-amine

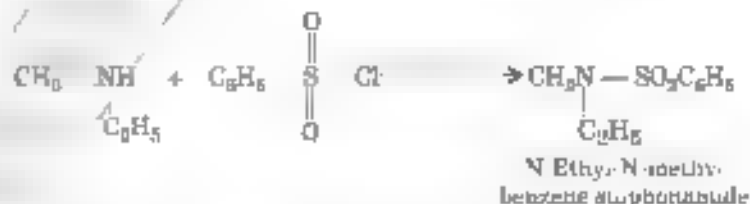
Q.15. Write down the IUPAC name of

Ans. N,N-Dimethylaniline

Q.16. A compound Z with molecular formula $\text{C}_8\text{H}_9\text{N}$ reacts with $\text{C}_6\text{H}_5\text{SO}_2\text{Cl}$ to give a solid, insoluble in alkali. Identify Z.

Ans. Z is an aliphatic amine which gives a solid insoluble in base. This means that reaction with $\text{C}_6\text{H}_5\text{SO}_2\text{Cl}$ must give a product without any replaceable hydrogen attached to nitrogen. Therefore, the amine must be a secondary amine. Hence, Z is ethylmethylamine.

Hence,

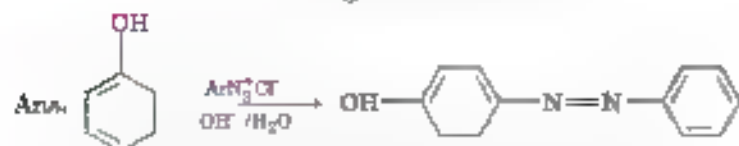
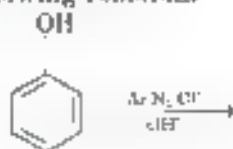


Q.17. A primary amine, RNH_2 can be reacted with $\text{CH}_3\text{--X}$ to get secondary amine, $\text{R--NH(CH}_3\text{)}$ but the only disadvantage is that 3° amine and quaternary ammonium salts are also obtained as side products. Can you suggest a method where RNH_2 forms only 2° amine?

Ans. $\text{RNH}_2 \xrightarrow{\text{KOH/CHCl}_3} \text{RNC} \xrightarrow{\text{H}_2, \text{Pd}} \text{RNHCH}_3$

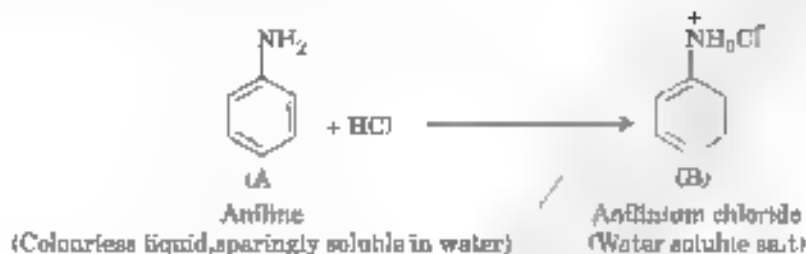
Carbonylamine reaction is shown by 1° amines only which results in the replacement of two hydrogen atoms attached to nitrogen atom of NH_2 group by one carbon atom. On catalytic reduction, the isocyanide forms a secondary amine with one methyl group.

Q.18. Complete the following reaction.

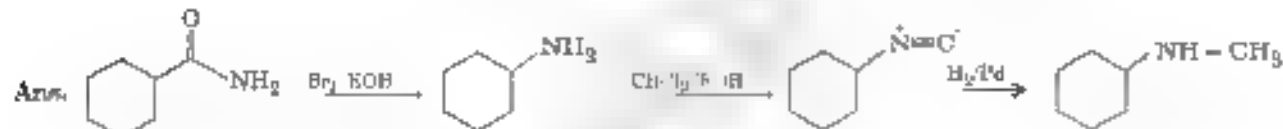
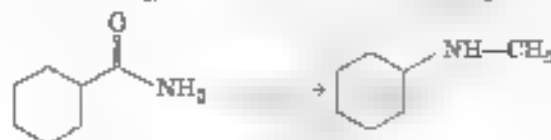


Q.19. Why is aniline soluble in aqueous HCl?

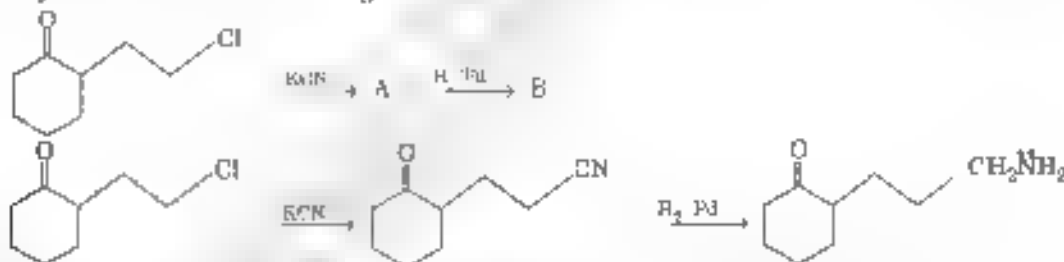
Ans. Aniline forms the salt anilinium chloride with HCl^+ which is water soluble



Q.20. Suggest a route by which the following conversion can be accomplished

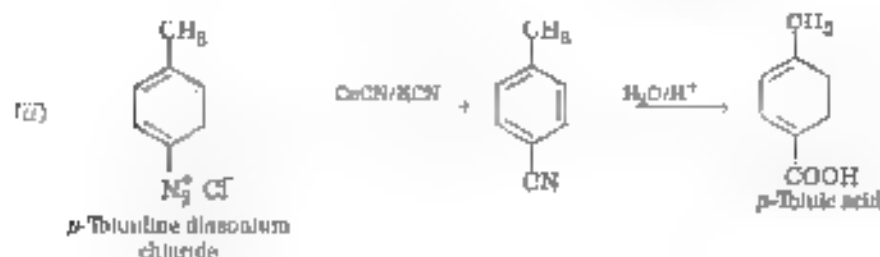
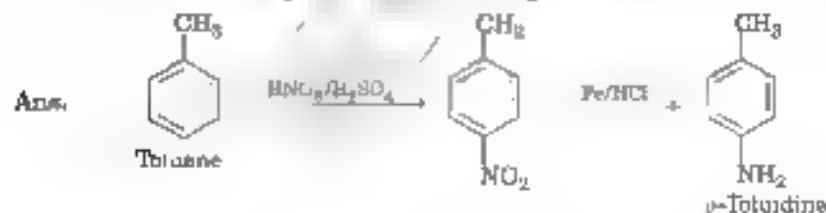


Q.21. Identify A and B in the following reaction.



Q.22. How will you carry out the following conversions?

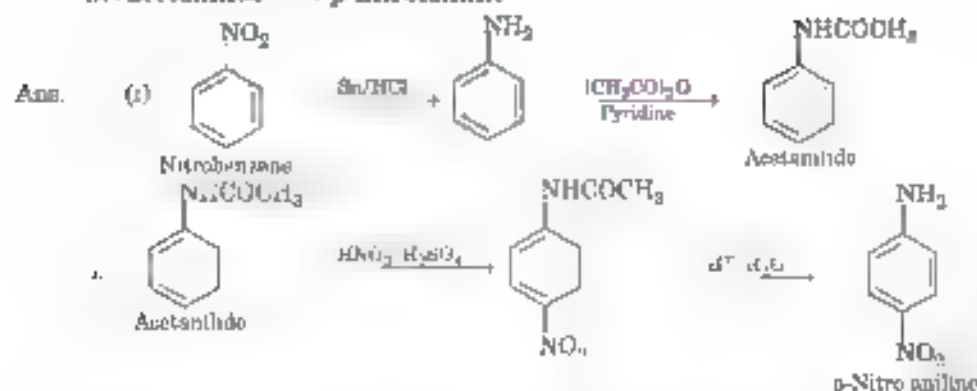
(i) Toluene \rightarrow p-toluidine (ii) p-toluidine diazonium chloride \rightarrow p-toluic acid



Q.23. Write following conversions:

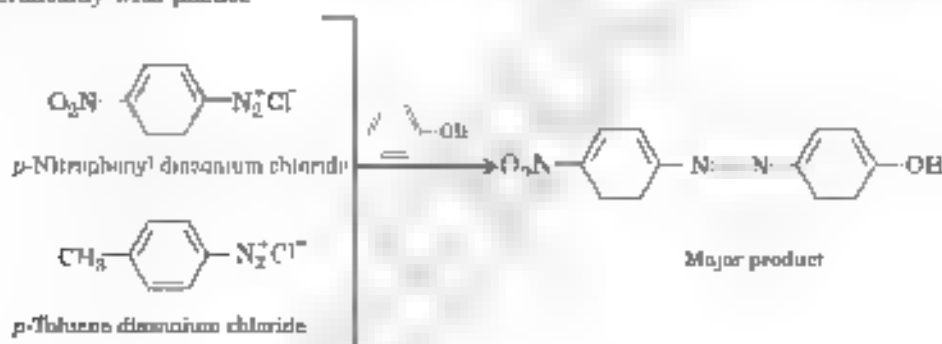
(i) nitrobenzene \rightarrow acetanilide

(ii) acetanilide \rightarrow *p*-nitroaniline

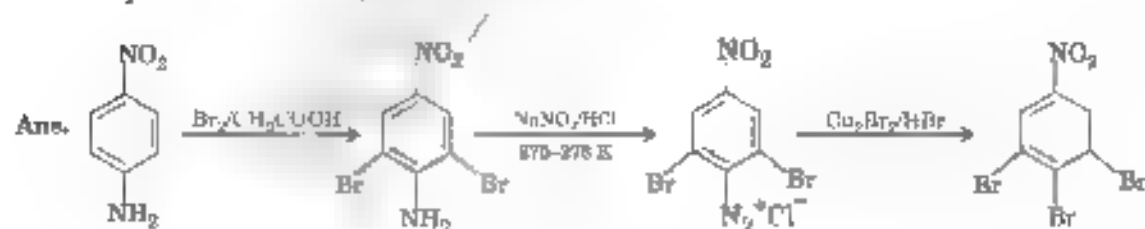
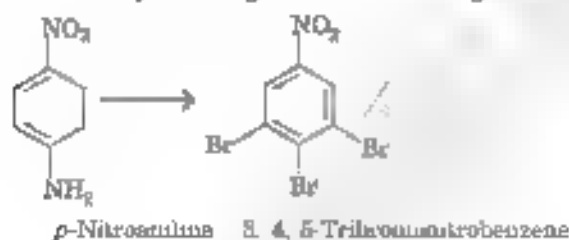


Q.24. A solution contains 1 g mol. each of *p*-toluene diazonium chloride and *p*-nitrophenyl diazonium chloride. To this 1 g mol. of alkaline solution of phenol is added. Predict the major product. Explain your answer.

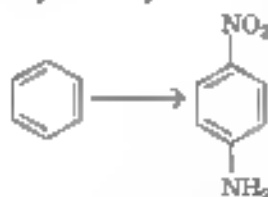
Ans. This reaction is an example of electrophilic aromatic substitution. In alkaline medium, phenol forms phenoxide ion which is more electron rich than phenol and hence more reactive for electrophilic attack. The electrophile in this reaction is aryl diazonium cation. *p*-Nitrophenyldiazonium cation is a stronger electrophile than *p*-toluene diazonium cation. Therefore it couples preferentially with phenol.

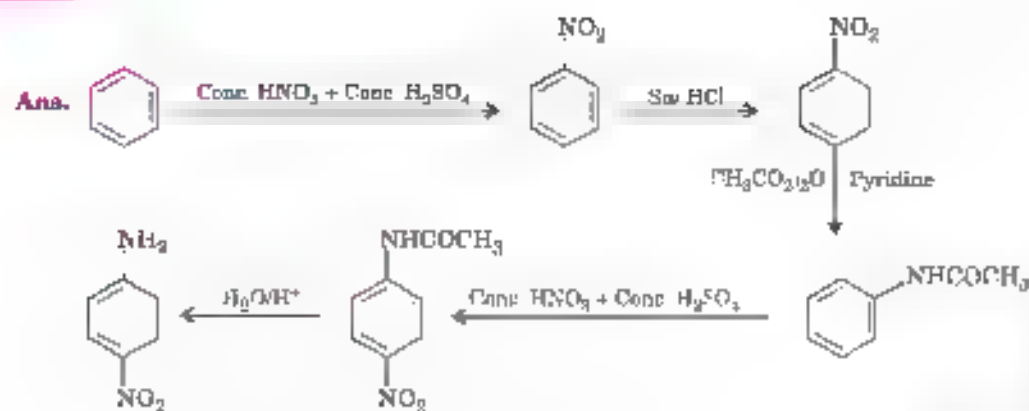


Q.25. How will you bring out the following conversion?

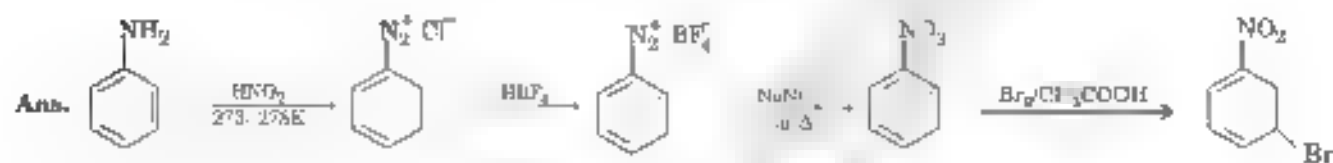
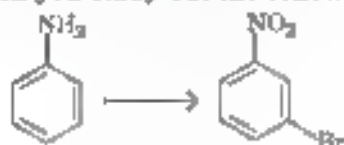


Q.26. How will you carry out the following conversion?

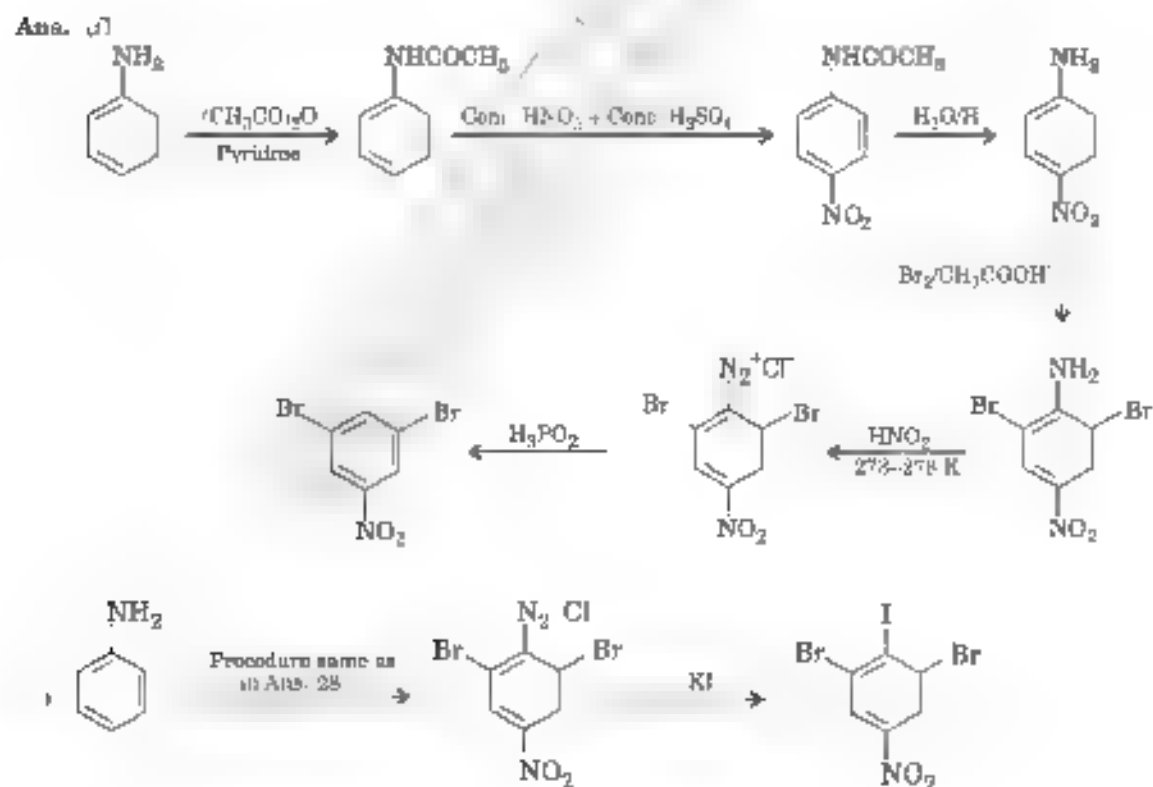
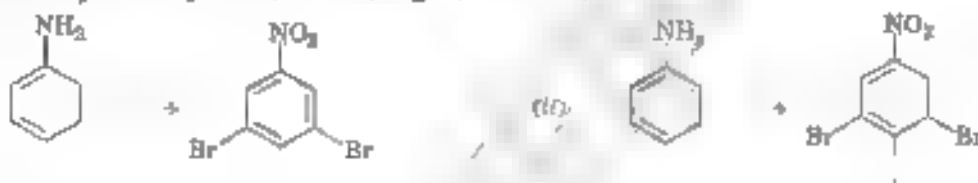




Q.27. How will you carry out the following conversion?



Q.28. How will you carry out the following conversions?




QUICK

MEMORY TEST



A. Say True or False

1. Amines act as Lewis bases.
2. In aqueous solution, trimethylamine is more basic than methylamine.
3. *p*-Bromoaniline is formed when aniline is treated with bromine water.
4. Azo dye test can be used to distinguish aromatic primary amines from aliphatic primary amines.
5. Catalytic reduction of carbylamines always gives primary amines.
6. *N*-Methylbenzamide on heating with aqueous solution of NaOH and Br₂ gives *N*-methylaniline.
7. Secondary amines evolve N₂ with nitrous acid.
8. Acetanilide is less basic than aniline.
9. Gabriel phthalimide synthesis is used for the preparation of aromatic primary amines.
10. Tertiary amines dissolve in nitrous acid to form corresponding salts.

B. Complete the missing links

1. Aniline on heating with fuming H₂SO₄ gives _____.
2. The IUPAC name of lowest molecular mass tertiary amine is _____.
3. In Schotten-Baumann reaction, aniline is heated with _____.
4. Carbylamine test is used to test _____ amines.
5. Libermann nitroso reaction is used for the detection of _____ amines.
6. Hinsberg reagent is _____.
7. Phenyl isocyanide on reduction with hydrogen and Raney nickel gives _____.
8. Secondary amines react with aldehydes and ketones containing α -hydrogen to form _____.
9. Reaction of acetanilide with NaOH and Br₂ gives _____.
10. In Hoffmann bromamide reaction, the carbonyl group is lost as _____.

11. $\text{CH}_3\text{CH}_2\text{CONH}_2 + 4\text{H} \xrightarrow[\text{ether}]{\text{LiAlH}_4} \text{_____} + \text{_____}$
12. $\text{C}_6\text{H}_5\text{NHCH}_3 + \text{H}_2\text{SO}_4 \rightarrow \text{_____}$
13. $\text{C}_2\text{H}_5\text{NH}_2 + \text{_____} \xrightarrow[\text{_____}]{\text{aq. NaOH}} \text{C}_2\text{H}_5\text{NHC}_6\text{H}_5 + \text{HCl}$
14. $\text{R}_2\text{NH} + \text{Cl}-\text{C}(=\text{O})-\text{Cl} \rightarrow \text{_____} + \text{_____}$
15. $\text{C}_6\text{H}_5\text{N}_2^+\text{Cl}^- + \text{CH}_3\text{CH}_2\text{OH} \rightarrow \text{_____} + \text{_____}$

C. Choose the correct alternative

1. Isocyanide test is used for the detection of primary/secondary amines.
2. Amino group is *ortho*-*para*/*meta* director.
3. Primary/tertiary amines do not react with Hinsberg's reagent.
4. Out of aniline and benzylamine, aniline/benzylamine gives azo dye test.
5. On treating benzene diazonium chloride with hypophosphorous acid, the product is phenol/benzene.
6. pK_b of aniline is less/more than $p\text{-C}_6\text{H}_4\text{NH}_2/\text{NH}_3$.
7. K_b of *p*-methylaniline is more/less than aniline.
8. Aniline is less/more basic than ethylamine.
9. Electron withdrawing group on aniline makes it less/more basic.
10. Gabriel phthalimide synthesis is used for the preparation of primary aromatic/primary aliphatic amines.

Answers

QUICK

MEMORY TEST

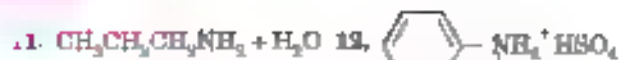


A. Say True or False

1. True 2. False
3. False 4. *p*-Tribromoaniline is formed.
4. True
5. False : Give secondary amines.
6. False : Secondary amines do not undergo Hoffmann bromamide reaction.
7. False 8. True 9. False 10. True

B. Complete the missing links

1. Sulphanilic acid
2. *N,N*-Dimethylmethanamine
3. benzoyl chloride
4. primary
5. secondary
6. benzene sulphonyl chloride
7. *N*-methylaniline
8. enamines
9. methylaniline
10. carbonate ion



Choose the correct alternative

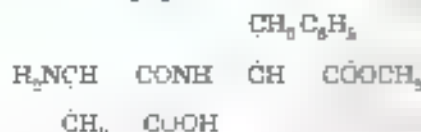
- | | | |
|-----------------------|---------------|-------------|
| 1. primary | 2. ortho-para | 3. tertiary |
| 4. aniline | 5. benzene | 6. more |
| 7. more | 8. less | 9. less |
| 10. primary aliphatic | | |

HOTS

Higher Order Thinking Skills & Advanced Level

QUESTIONS WITH ANSWERS

Q.1. Aspartame, an artificial sweetener, is a peptide and has the following structure

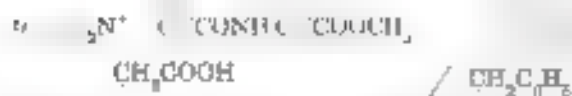
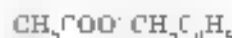


- (i) Identify the four functional groups.
 (ii) Write the zwitter ionic structure.
 (iii) Write the structures of the amino acids obtained from the hydrolysis of aspartame.
 (iv) Which of the two amino acids is more hydrophobic? /

(L.T. 2001)

Ans. (i) The four functional groups are

- (a) NH_2 (amino group) (b) $-\text{CONH}-$ (peptide or amide group)
 (c) $-\text{COOH}$ (carboxylic group) (d) $-\text{COOCH}_3$ (ester group)



(iv) $\text{H}_2\text{N}-\text{CH}_2-\text{COOH}$ will be more hydrophobic due to bulky alkyl groups

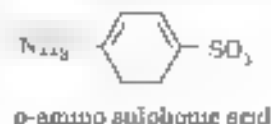
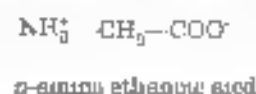
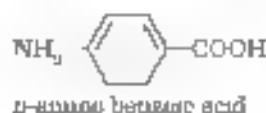
Q.2. *tert*-Butylamine cannot be prepared by action of ammonia on *tert*-butyl bromide. Why? Explain.

Ans. *tert*-Butylamine is a 3° alkyl amine. On treatment with a base like NH_3 , it prefers to undergo elimination reaction rather than substitution. Therefore the product is isobutylene instead of *tert*-butylamine.



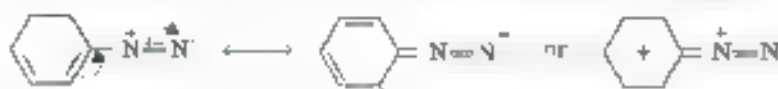
Q.3. Explain 3-aminoethanoic acid exists as a dipolar ion as does *p*-amino sulphonic acid but *p*-amino benzoic acid does not

Ans. The aliphatic $-\text{NH}_2$ group is sufficiently basic to accept an H^+ from COOH group. The COOH group is not strong enough to donate H^+ to the weakly basic ArNH_2 , but SO_3H group sufficiently strong enough to donate H^+ to weakly basic ArNH_2 .



Q.4. Why are aryl diazonium ion more stable than alkyl diazonium ion ?

Ans. The stability of aryl diazonium ion is due to resonance or electron release from *o*- and *p*-positions of the ring



This type of resonance stability is not possible in alkyl diazonium ion.

Q.5. *p*-methoxyaniline is a stronger base than aniline but *p*-nitroaniline is a weaker base than aniline. Explain.

Ans. Methoxy group $-\text{OCH}_3$ is electron releasing group and increases the electron density on N atom. Therefore, it has greater electron donating tendency than aniline and thus is a stronger base than aniline. On the other hand, nitro group is electron withdrawing group and, therefore, decreases the electron density on nitrogen atom. As a result, *p*-nitroaniline is a weaker base than aniline.

Q.6. Can we prepare aniline by Gabriel phthalimide reaction ?

Ans. Aniline cannot be prepared by Gabriel phthalimide reaction because it requires the treatment of potassium phthalimide with $\text{C}_6\text{H}_5\text{I}$ or $\text{C}_6\text{H}_5\text{Br}$. Since aryl halides do not undergo nucleophilic substitution reactions under ordinary conditions, therefore, the reaction does not occur. Hence, aniline cannot be prepared by this method.

Q.7. Sulphanilic acid is insoluble in water and organic solvents. Explain.

Ans. Sulphanilic acid is ionic in nature and, therefore, it is insoluble in organic solvents. Its solubility in water is typical of dipolar salts. Not all such salts dissolve in water.



Q.8. Why is an amide more acidic than amine ?

Ans. The amide has the following resonating structures



Due to the delocalisation of lone pair of electrons on N, $\text{C}=\text{N}^+-$ group, amino group acquires a positive charge which makes N-H bond weak. Moreover, the anion formed after removal of a proton is also stabilized by resonance as



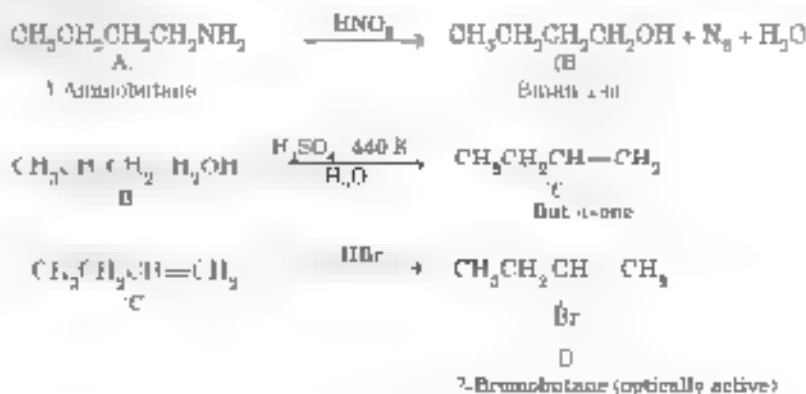
However, no such stabilization is possible in amines.

Q.9. Which is more basic PhNH_2 or Ph_2NH ?

Ans. Aromatic amines are less basic than alkylamines because the electron density of the lone pair of electrons is delocalized into the ring, mainly at ortho and para positions. Increase in number of phenyl groups bonded to N increases delocalization and hence decreases basicity. Therefore, PhNH_2 is more basic than Ph_2NH .

Q.10. An optically inactive compound (A) having molecular formula $\text{C}_4\text{H}_9\text{N}$ on treatment with HNO_2 gave an alcohol (B). (B) on heating at 440 K gave an alkene (C). (C) on treatment with HBr gave an optically active compound (D) having the molecular formula $\text{C}_4\text{H}_9\text{Br}$. Identify A, B, C and D and write down their structural formulae. Also write equations involved.

Ans. Since compound (A) is optically inactive and contains nitrogen which gives alcohol with HNO_2 , it is primary amine. The reactions may be given as

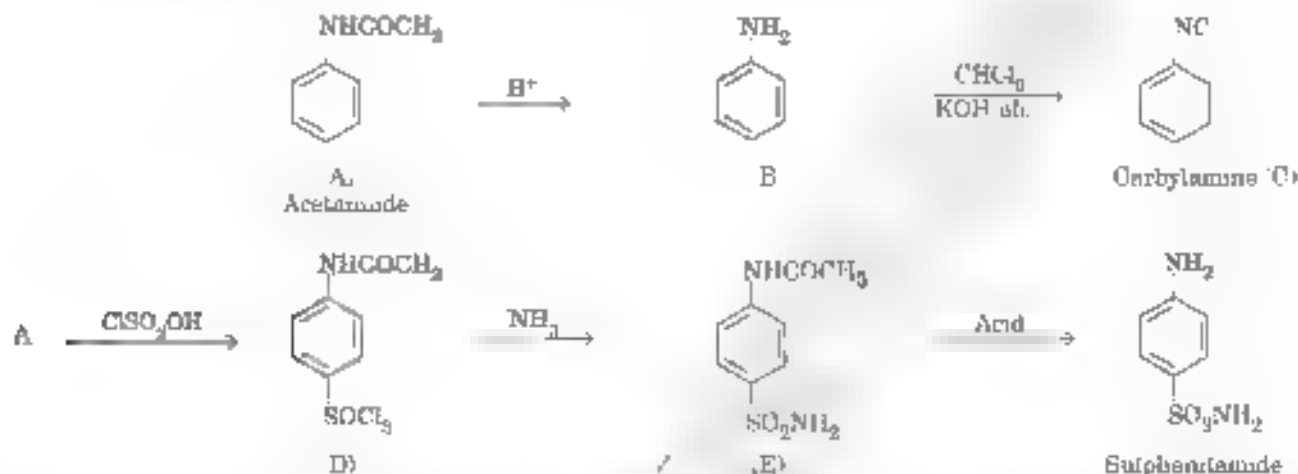


Q.11. A colourless substance (A) is sparingly soluble in water and gives (B) on heating with mineral acids. Compound (B) on reaction with CHCl_3 and alcoholic potash produces an obnoxious smell of carbonylamine due to the formation of (C). Compound A on reaction with chlorosulphonic acid gives (D) which on treatment with ammonia gives (E). Compound (E) on hydrolysis gives sulphanilamide; a well known drug. Give structures of A to E) with proper reasoning.

Ans. The reaction of B with chloroform and alcoholic KOH gives carbonylamine. This indicates that B is a primary aromatic amine. Since sulphanilamide is the final product, it means that B is aniline.

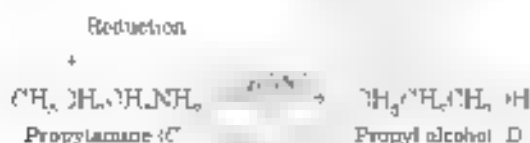
Now B is formed by the acidic hydrolysis of A which is colourless and sparingly soluble in water therefore, A is acetanilide.

The reactions may be explained as

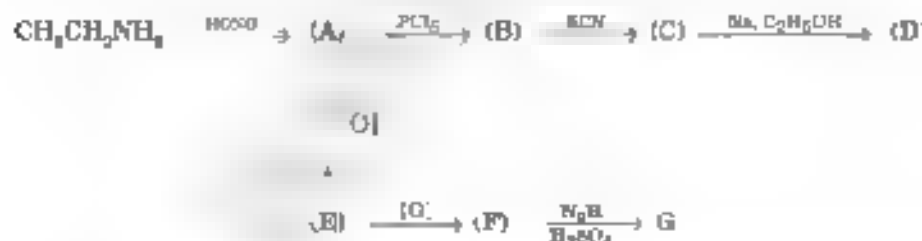


Q.12. An organic compound A ($\text{C}_3\text{H}_5\text{N}$) on boiling with alkali gives ammonia and sodium salt of an acid B ($\text{C}_3\text{H}_5\text{O}_2$). A on reduction gives C ($\text{C}_3\text{H}_9\text{N}$) which with nitrous acid gives D ($\text{C}_3\text{H}_7\text{O}$). Give the structural formulae of A, B, C and D.

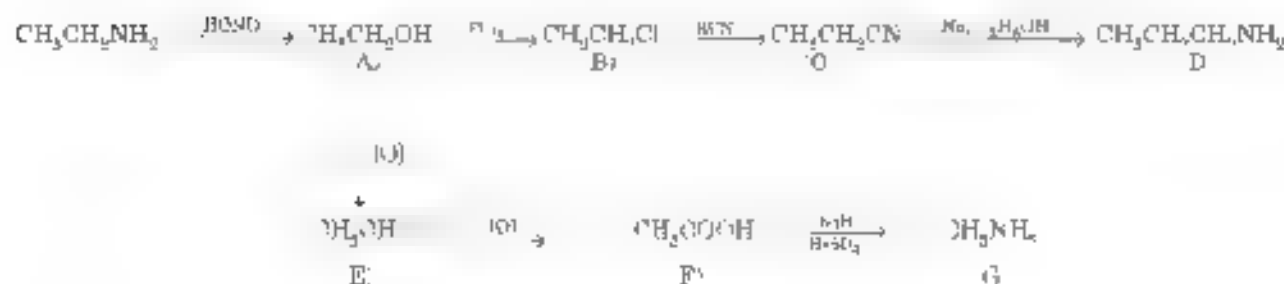
Ans. The chemical reactions are



Q.13. Identify (A) to (G) in the following reaction scheme



Ans.





(X)

Tertiary alcohol

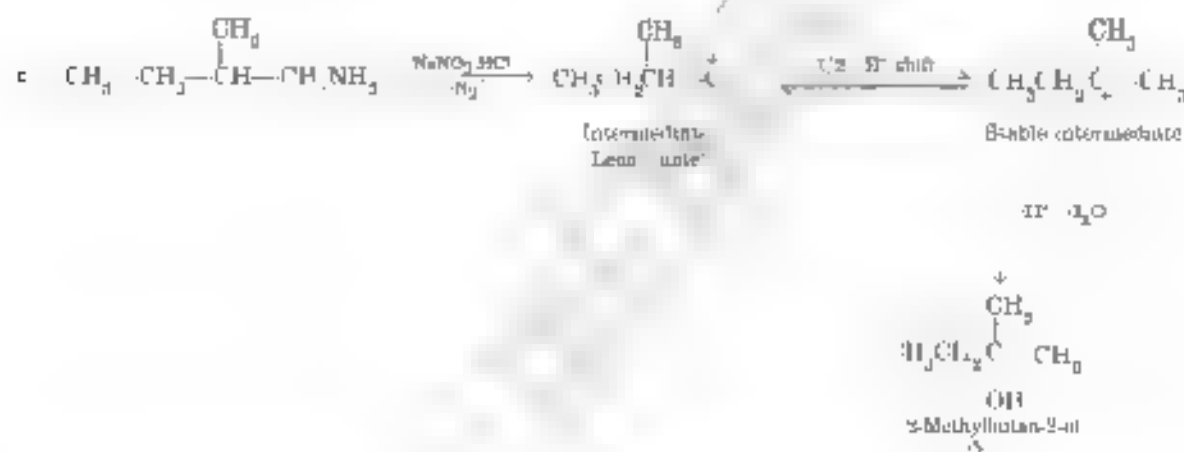
Optically active

- Identify (X) and (Y)
- Is (Y) optically active?
- Give structures of intermediates if any in the formation of (X) to (Y)

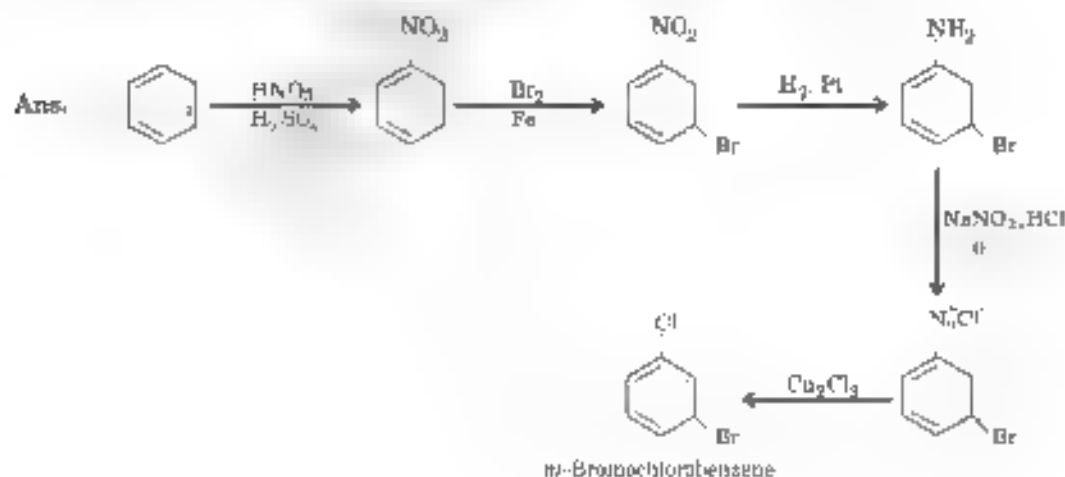
Ans. a. Since compound X on treatment with NaNO_2/HCl evolves N_2 gas, it must be a primary amine. Further since X is optically active, it must contain a chiral carbon. The $-\text{NH}_2$ cannot be directly attached to a chiral carbon because such amines readily undergo racemization due to nitrogen inversion. Therefore, the structure of X is



b. No, Y is not optically active



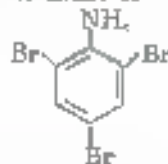
Q.15. Starting with benzene and using suitable reagents, outline the synthesis of
 (i) *m*-bromochlorobenzene (ii) *p*-dinitrobenzene (iii) *m*-bromotodobenzene



16. What happens when benzene diazonium chloride solution is added slowly to boiling dil. mineral acid?

Meghalaya S.B. 2015

17. Write the IUPAC name of



D.S.B. 2016

18. How is benzamide converted into benzylamine?

Pb S.B. 2018

19. Write down diazotisation reaction.

(Pb. S.B. 2017)

20. Complete the following reaction



(Mizoram S.B. 2018)

21. Write down Hinsberg's test for primary amines

Pb. S.B. 2017

22. Write IUPAC name of the following compound



D.S.B. 2017

23. Write IUPAC name of the following compound:

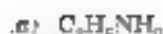


D.S.B. 2017 Hr. S.B. 2018

24. Write in the increasing order of basicity of the following



Hr.S.B. 2018



Hr. S.B. 2013

24. $\text{C}_6\text{H}_5\text{N}_2\text{Cl} + \text{CuCN} \rightarrow \text{C}_6\text{H}_5\text{CN} + \text{N}_2 + \text{CuCl}$ is

a) Balz-Schiemann

(b) Gattermann reaction

c) Simonini reaction

d) Sandmeyer reaction

Hr. S.B. 2013

25. Which of the following is most basic?

(a) Benzylamine

(b) Aniline

c) Acetanilide

(d) p-nitroaniline

Hr. S.B. 2013, 2016

26. Among the following which one is strongest base?

a) Ammonia

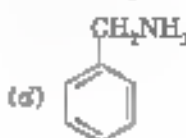
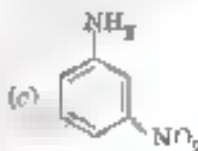
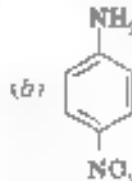
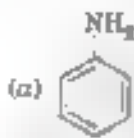
(b) Methylamine

c) Ethylamine

(d) None of these

Uttarakhand S.B. 2013

27. Which of the following compound is the most basic?



West Bengal S.B. 2018

28. The IUPAC name of $\text{CH}_3\text{-N(CH}_3\text{)-CH}_2\text{CH}_3$ is



a) N-Ethyl-N-methylbenzenamine

b) N-Methyl-N-ethylbenzenamine

c) N,N-Ethyl methyl benzenamine

d) N,N-Methyl ethyl benzenamine

Mizoram S.B. 2014

29. Gabriel phthalimide reaction is used for the preparation of

(a) 1° amine

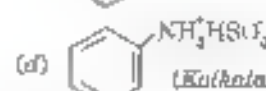
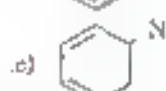
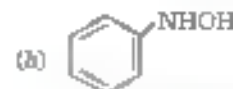
(b) 2° amine

(c) 3° amine

(d) all of these

Uttarakhand S.B. 2016

30. Which of the following compound will be formed when aniline reacts with H_2SO_4 ?



(Kolkata S.B. 2016)

31. Which one of the following is most basic?



H.P.S.B. 2016

32. $\text{C}_6\text{H}_5\text{NH}_2 + \text{HNO}_3 \rightarrow \text{A}$, A is

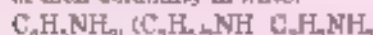


CBSE QUESTIONS

25. Why do amines react as nucleophiles?

A.I.S.B. 2003, C.B. S.E. Sample paper 2017

26. Arrange the following compounds in the increasing order of their solubility in water



A.I.S.B. 201 D.S.B. 2014

27. Give a chemical test to distinguish between ethylamine and aniline.

A.I.S.B. 2011

28. Arrange the following in an increasing order of their basic strength



A.I.S.B. 2011, Hr. S.B. 2013

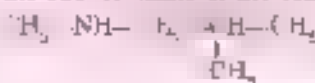
29. Write the structure of N-methylethanamine.

A.I.S.B. 2013

30. The conversion of primary organic amine into diazonium salts is known as

A.I.S.B. 2014

31. Write the IUPAC name of the compound



A.I.S.B. 2016

MCQs. from State Boards' Examinations

32. When a primary amine reacts with chloroform in ethanolic KOH, then the product is

a) isocyanide

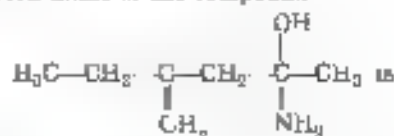
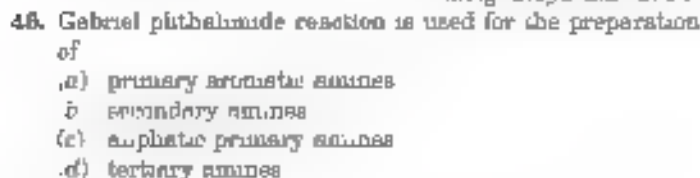
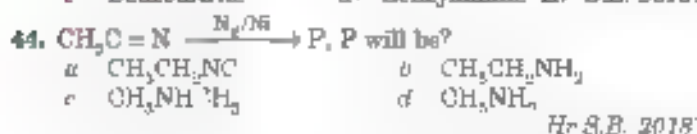
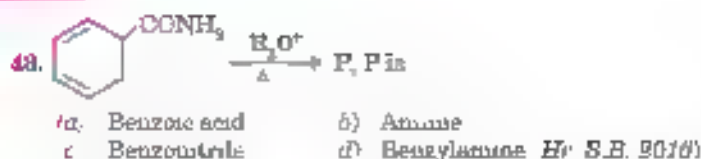
b) aldehyde

(c) cyanide

d) alcohol

Uttarakhand S.B. 2013

33. Which of the following does not react with Hinsberg reagent?



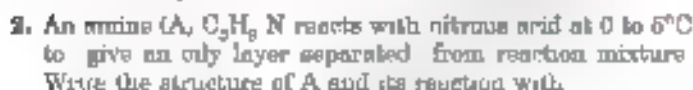
- (a) 2-Amino-4-ethyl-2-hydroxypent-4-ene
(b) 2-Amino-4-ethylpent-4-en-2-ol
(c) 4-Ethyl-2-hydroxypent-4-en-2-amine
(d) 2-Amino-4-methylhexan-2-ol

Mizoram S.B. 2018

Short Answer Questions (carrying 4 or 3 marks)

1. Explain the following

- (i) Tertiary amines do not undergo acylation.
(ii) CH_3NH_2 is stronger base than ammonia.
(iii) It is difficult to prepare pure amines by ammonolysis of alkyl halides.



- (i) acetyl chloride
(ii) methyl magnesium bromide



- (b) How can you find out whether a given amine is a primary amine? Write the chemical reaction involved in the test you perform.

H.P.S.B. 2008, Meghalaya S.B. 2018



- (i) In an increasing order of basic strength
 $C_2H_5NH_2$, $C_6H_5N(CH_3)_2$, $(C_2H_5)_2NH$ and CH_3NH_2
(ii) In a decreasing order of basic strength
Aniline, *p*-nitroaniline and *p*-toluidine
(iii) In an increasing order of pK_b values
 $C_2H_5NH_2$, $C_6H_5NHCH_3$, $(C_2H_5)_2NH$ and $C_6H_5NH_2$

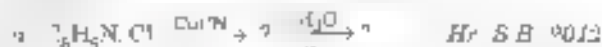
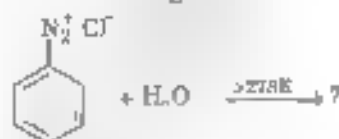
D.S.B. 2010



D.S.B. 2010



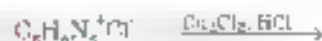
D.S.B. 2011



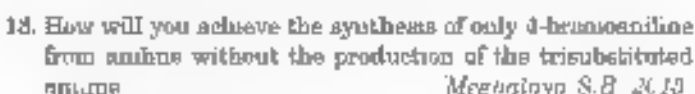
D.S.B. 2019



Mizoram S.B. 2013



H.P.S.B. 2019

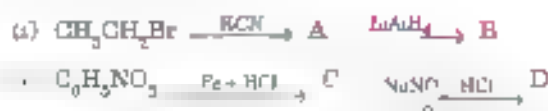


Meghalaya S.B. 2019

Or

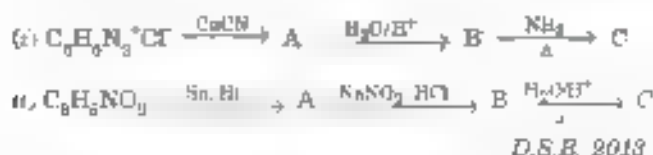


14. a. Identify A, B, C and D



b. Write one chemical test to distinguish between ethylamine and aniline. (Assam S.B. 2013)

15. Give the structures of A, B and C in the following reactions.



16. Write Hinsberg's test to distinguish primary, secondary and tertiary amines. (Uttarakhand S.B. 2014)

17. Discuss the effect of electron donating and electron withdrawing group on basicity of aromatic amines.

Or

Write short notes on the following.

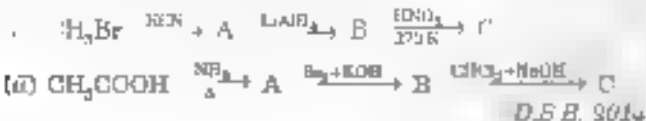
- Carbylamine reaction,
- Gabriel-phthalimide synthesis. (Hr S.B. 2013)

18. How will you convert the following

- Nitrobenzene into aniline
- Ethanoic acid into methanamine
- Aniline into N-phenylethanamide.

(Write the chemical equations involved. (D.S.B. 2014)

19. Give the structures of A, B and C in the following reactions:



20. Give chemical equations for the following reactions:

- Gatterman Reaction
- Carbylamine reaction
- Ammonolysis

Hr S.B. 2013

21. (a). What is Hoffmann's bromamide reaction? Write the reaction involved in it.

(b) Secondary amine is stronger base than tertiary amine. Give reason.

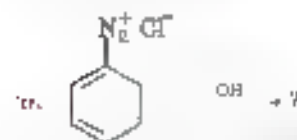
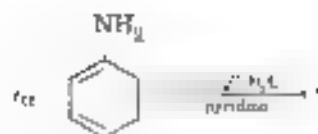
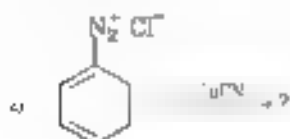
(c) Complete the following reactions



22. Write the following name reactions with chemical equations.

- Ammonolysis
- Hoffmann bromamide reaction
- Coupling reaction. (Uttarakhand S.B. 2013)

23. Complete the following reactions



Hr S.B. 2013

24. (a). Give chemical tests to distinguish between primary, secondary and tertiary amines?

(b) Give reasons for the following

- $\text{C}_6\text{H}_5\text{NH}_2$ is a stronger base as compared to aniline
- Aniline does not show Friedel-Crafts reaction.

Hr S.B. 2013

25. (a). How will you convert aniline to benzene?

(b). Write the following reactions:

- Baiz Schiemann reaction
- Carbylamine reaction

Diazotisation (Ph. S.B. 2015)

26. (a). Account for the correct order of decreasing basicity of ethylamine, 1-aminoethanol and 3-amino propan-1-ol.

(b) How will you convert aniline into chlorobenzene?

(c) Write a short note on carbylamine test

Or

(a). Write coupling reaction.

(b) Give a chemical test to distinguish between aniline and N-methylaniline

(c) How will you convert benzoic acid to aniline?

H.P.S.B. 2016

27. (a) Tertiary amines do not undergo acylation. Explain?

(b) Write a short note on Hoffmann's degradation reaction

(c) How will you convert aniline into benzene diazonium chloride?

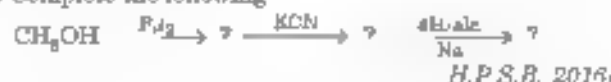
Or

(a). Write diazotisation reaction

(b) Aromatic amines cannot be prepared by Gabriel phthalimide synthesis. Explain.

(c) How will you convert methylamine into ethylamine?

(d) Complete the following



28. (a). Give a chemical test to distinguish between the following pair of compounds

Methylamine and ethylamine

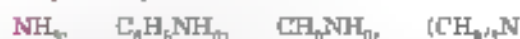
(b) How will you convert benzene to aniline?

(c) Write a short note on Gabriel phthalimide synthesis.

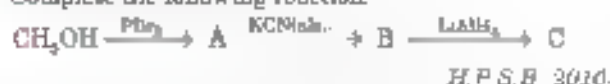
Or

(a). Write a short note on ammonolysis reaction

- (b) Aniline does not undergo Friedel Crafts alkylation. Explain.
 (c) Arrange the following compounds in order of their basic strength in aqueous solution.



- (d) Complete the following reaction.



20. (a) Account for the following observations.

- (i) Aniline does not undergo Friedel Crafts reactions.
 (ii) pK_b for aniline is more than that for methylamine

- (b) Give a chemical test to distinguish between methylamine and dimethylamine. (Hr. S.B. 2010.)

21. (a) Why is secondary amine more basic than the tertiary amine?

- (b) How can 1° 2° and 3° amine be distinguished by I Linsberg test?

- (c) Complete the reaction.

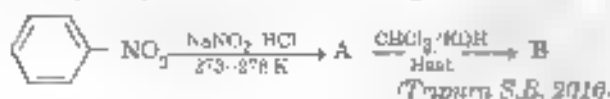


Nagaland S.B. 2018.

21. (a) Arrange the following compounds in an increasing order of basic strength in their aqueous solutions.



- (ii) Identify the products in the following reaction.



22. Identify A, B, C and D in the following conversion:



23. Complete the following reactions



24. Write the structures of A, B and C in the following



25. (i) Arrange the following in decreasing order of their basic strength.



- (ii) Identify the organic product in the following reaction. Give its IUPAC name.



26. (i) Arrange the following amines in order of increasing their basic strength.



- (ii) How do aliphatic primary amines react with nitrous acid? Give equation. (Meghalaya S.B. 2017)

27. (i) Write the major product of the following reaction.



- (ii) Write the products formed when aniline undergoes direct nitration. (Meghalaya S.B. 2017)

28. Give the chemical equations for each of the following reactions



29. What are diazonium salts?

How is nitrobenzene converted to benzenediazonium chloride? (Manipur S.B. 2017)

40. (a) Write a note on Hoffmann bromamide reaction giving an able chemical reaction.

- (b) Tertiary amines are stronger bases than primary amines. Why? / (Mizoram S.B. 2017)

41. (a) What happens when aniline reacts with bromine water at room temperature?

- (b) Give a chemical test for primary amines.

- (c) Write the diazotisation reaction of aniline.

Assam S.B. 2018

42. (a) Aromatic amines are stronger base than aliphatic amines. Explain.

- (b) Toluene is more easily nitrated than benzene. Explain.

- (c) Discuss the deactivating *m*-directing nature of nitro group. (Hr. S.B. 2017)

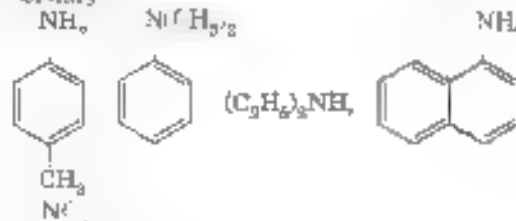
43. (a) Why are aliphatic amines stronger base than the aromatic amines?

- (b) What is carbylamine reaction? Give the reaction.

- (c) Give one test to distinguish primary, secondary and tertiary amines from each other.

(Nagaland S.B. 2017)

44. (a) Classify the following amines as primary, secondary and tertiary.



Identify the products B and C and write their formulae. (Kerala S.B. 2017)

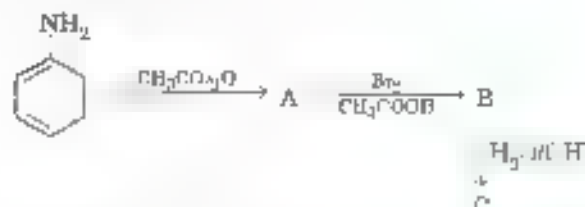
45. Identify the compounds X, Y and Z in the following reactions



46. (a) Explain, with the help of chemical equations, how the following compounds would be obtained from benzene diazonium chloride.

- i) Iodobenzene
ii) 4-Aminodiazobenzene

- b) Complete the following reaction.



- c) What will happen if aniline is treated with aqueous bromine? (Hogborge S.B. 2018)
47. (a) Explain carbylamine reaction with equation.
b) How does nitrobenzene is reduced to aniline? Give equation.
c) Write the IUPAC name of $\text{C}_6\text{H}_5\text{—N—CH}_3$



48. (a) Name the test used to identify primary amines using CHCl_3 and ethanoic KOH
b) How can you convert methyl iodide to ethanamine? (Kerala S.B. 2018)

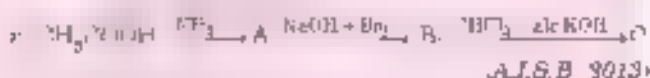
CBSE QUESTIONS

49. Account for the following observations:
(a) pK_b of aniline is more than that of methylamine.
(b) Methylamine solution in water reacts with ferric chloride solution to give a precipitate of ferric hydroxide.
(c) Aniline does not undergo Friedel-Crafts reaction. (A.I.S.B. 2008, D.S.B. 2008)
50. Write one chemical reaction each to illustrate the following:
i) Hoffmann's bromamide reaction
ii) Gabriel phthalimide synthesis (A.I.S.B. 2008)
51. (a) Arrange the following compounds in an increasing order of basic strengths in their aqueous solutions:
 NH_3 , CH_3NH_2 , CH_3NHCH_3 , $\text{H}_2\text{NCH}_2\text{NHC}_6\text{H}_5$
(b) Complete the following reaction equations:
i) $\text{RCONH}_2 \xrightarrow[\text{I}_2/\text{NaOH}]{\text{NaOH}}$?
ii) $\text{C}_6\text{H}_5\text{N}_2\text{Cl} + \text{H}_2\text{PO}_3 + \text{H}_2\text{O} \rightarrow$?
(iii) $\text{C}_6\text{H}_5\text{NH}_2 + \text{Br}_2 (\text{aq}) \rightarrow$? (A.I.S.B. 2009)
52. Give the chemical tests to distinguish between the following pairs of compounds:
i) Ethylamine and aniline
ii) Aniline and benzylamine (A.I.S.B. 2010)

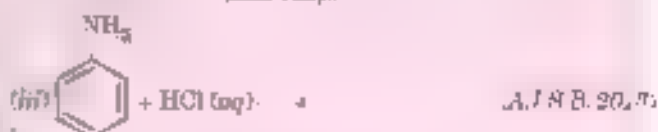
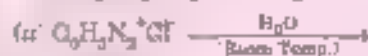
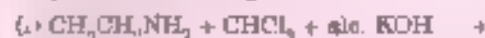
53. Give chemical tests to distinguish between the following pairs of compounds:
i) Methylamine and Dimethylamine
ii) Aniline and N-Methylaniline (A.I.S.B. 2010)

54. Describe the following giving the relevant chemical equation in each case:
i) Carbylamine reaction
ii) Hoffmann bromamide reaction (A.I.S.B. 2012, Hr S.B. 2018)

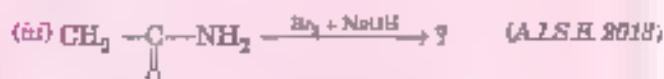
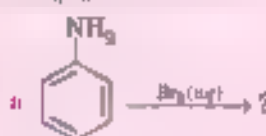
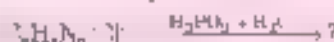
55. Give the structures of the products A, B and C in the following reactions:



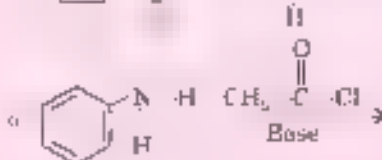
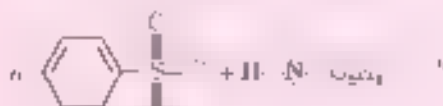
56. Complete the following reactions:



57. Write the main products of the following reactions:

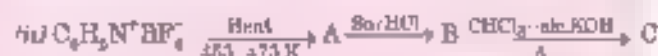
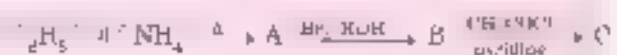


58. Write the main products of the following reactions:



(A.I.S.B. 2019)

59. Write the structures of A, B and C in the following:



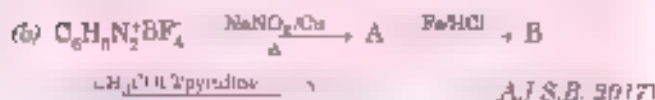
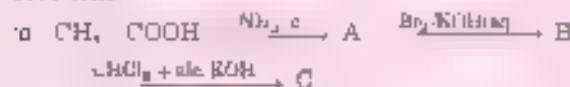
(A.I.S.B. 2016)

Q0. Give reasons.

- Acetylation of aniline reduces its activation effect.
- CH_3NH_2 is more basic than $\text{C}_6\text{H}_5\text{NH}_2$.
- Although NH_2 is *o/p* directing group, yet aniline on nitration gives a significant amount of *m*-nitroaniline.

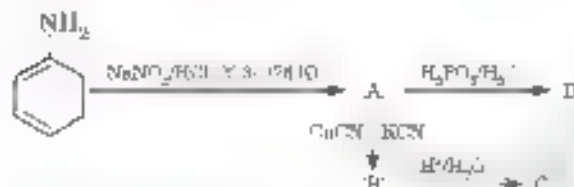
(D.S.B. 2017 A.J.S.B. 2017)

Q1. Write the structures of compounds A, B and C in the following reactions.

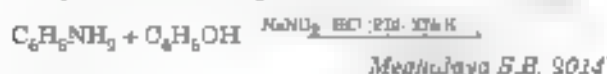


Long Answer Questions — (Carrying 5 marks)

- Explain why aniline does not undergo Friedel-Crafts reaction?
 - Identify the compounds A and B in the following sequence of reactions:



- Why are aliphatic amines more basic than aromatic amines?
- Why aromatic primary amines cannot be prepared by Gabriel phthalimide synthesis?
- Complete the following reaction:



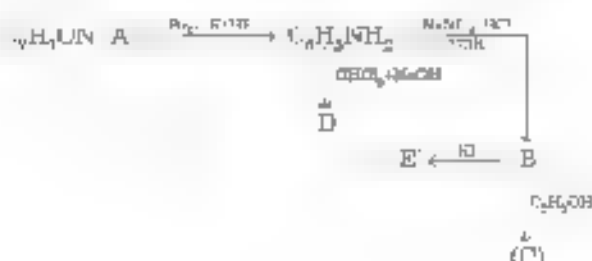
Q. (a) Why are alkylamines stronger base than arylamines?



c) What is diazotisation reaction?



Q. An aromatic compound 'A' of molecular formula $\text{C}_7\text{H}_7\text{ON}$ undergoes a series of reactions as shown below. Write the structures of A, B, C, D and E in the following reactions.



Or

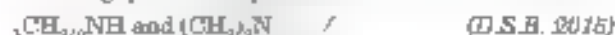
(a) Write the structures of main products formed when aniline reacts with the following reagents

- Br_2 water
- HCl
- $(\text{CH}_3\text{CO})_2\text{O}$ /pyridine

(b) Arrange the following in the increasing order of their boiling point



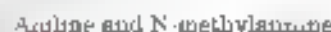
(c) Give a simple chemical test to distinguish between the following pair of compounds.



Q. (a) Illustrate the following reactions giving suitable example in each case

- Hofmann bromamide degradation reaction
- Diazotisation
- Gabriel phthalimide synthesis

(b) Distinguish between the following pairs of compounds



Or

(a) Write the structures of main products formed when benzene diazonium chloride $(\text{C}_6\text{H}_5\text{N}_2^+\text{Cl}^-)$ reacts with following reagents

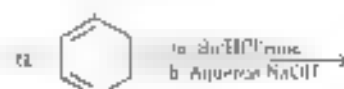
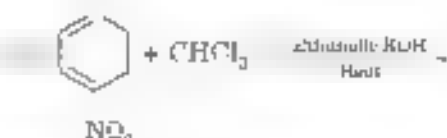
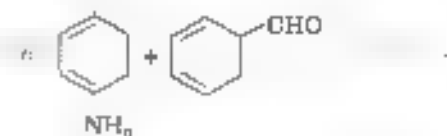
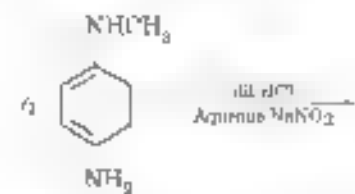


(b) Arrange the following



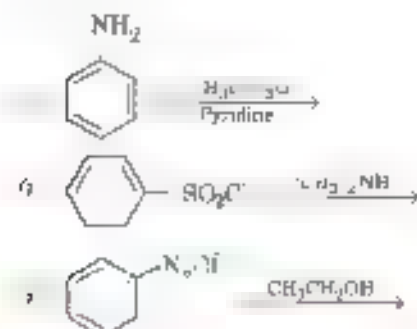
(a) Arrange *p*-nitroaniline, *p*-methylaniline in the increasing order of their basic strength. (A.J.S.B. 2015)

Q. Write the organic products in the following reactions:





11. (a) Write the structures of the main products of the following reactions



(b) Give a simple chemical test to distinguish between aniline and N,N-dimethylaniline.

(c) Arrange the following in the increasing order of their pK_b values.



(A.I.S.B. 2018)

Or

(a) Write the reactions involved in the following

(i) Hoffmann bromamide degradation reaction

(ii) Diazotisation

(iii) Gabriel phthalimide synthesis

(b) Give reasons.

(i) $(\text{CH}_3)_2\text{NH}$ is more basic than $(\text{CH}_3)_3\text{N}$ in an aqueous solution

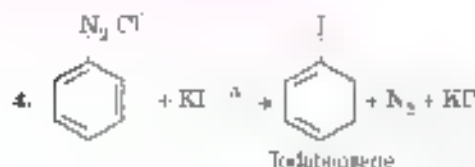
(ii) Aromatic diazonium salts are more stable than aliphatic diazonium salts. (A.I.S.B. 2018)

Hints & Answers

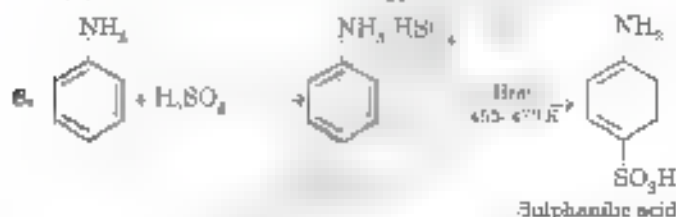
for Revision Exercises

▶ 1. Short Answer Question ◀

1. N,N-Dimethyl-3-methyl-3-pentanamine
2. $\text{CH}_3\text{CH}_2\text{NH}_2$ and CH_3NHCH_3
3. Sandmeyer reaction



6. $\text{ArN}_2\text{Cl} + \text{H}_3\text{PO}_2 + \text{H}_3\text{O}^+ \rightarrow \text{ArH} + \text{H}_3\text{PO}_3 + \text{HCl} + \text{N}_2$
7. 2,4,6-Tribromocaniline (white ppt)



9. Aniline is less basic than methylamine and therefore, its pK_b is more.
10. $\text{C}_6\text{H}_5\text{NH}_2 + \text{CHCl}_3 + 3\text{KOH} \xrightarrow{\text{Warm}} \text{C}_6\text{H}_5\text{NC} + 3\text{KCl} + 3\text{H}_2\text{O}$
11. p -nitroaniline < aniline < p -toluidine
12. $\text{CH}_3)_3\text{N} < \text{CH}_3\text{NH}_2 < (\text{CH}_3)_2\text{NH}$
14. $\text{H}_2\text{O}_2\text{NH}$



16. Phenol is formed

17. 4,4-Tribromocaniline



22. N-Methylpropan-2-amine

23. N-Ethyl-N-methylethanamine

24. $\text{C}_6\text{H}_5\text{NH}_2 < \text{C}_6\text{H}_5\text{CH}_2\text{NH}_2 < \text{C}_6\text{H}_5\text{NHCH}_3 < (\text{C}_6\text{H}_5)_2\text{NH}$

26. $\text{C}_6\text{H}_5\text{NH}_2 < (\text{C}_6\text{H}_5)_2\text{NH} < \text{C}_6\text{H}_5\text{NHCH}_3$

27. Aniline gives azo dye test while ethylamine does not give azo dye test.

28. $(\text{C}_6\text{H}_5)_3\text{N} < \text{C}_6\text{H}_5\text{NH}_2 < \text{C}_6\text{H}_5\text{N} < \text{CH}_3)_3\text{N} < \text{CH}_3\text{NH}_2$

29. $\text{CH}_3\text{CH}_2\text{NHCH}_3$

30. Diazotisation

31. N-Methyl-2-methyl propanamine.

- | | | | |
|--------|---------|---------|---------|
| 32. a) | 33. c) | 34. (d) | 35. (a) |
| 36. c) | 37. (d) | 38. (a) | 39. a |
| 40. d) | 41. c) | 42. (a) | 43. (a) |
| 44. b) | 45. a) | 46. (c) | 47. b |

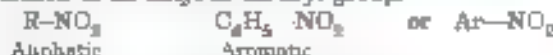
Competition File

Additional Useful Information and Objective Questions

ADDITIONAL USEFUL INFORMATION

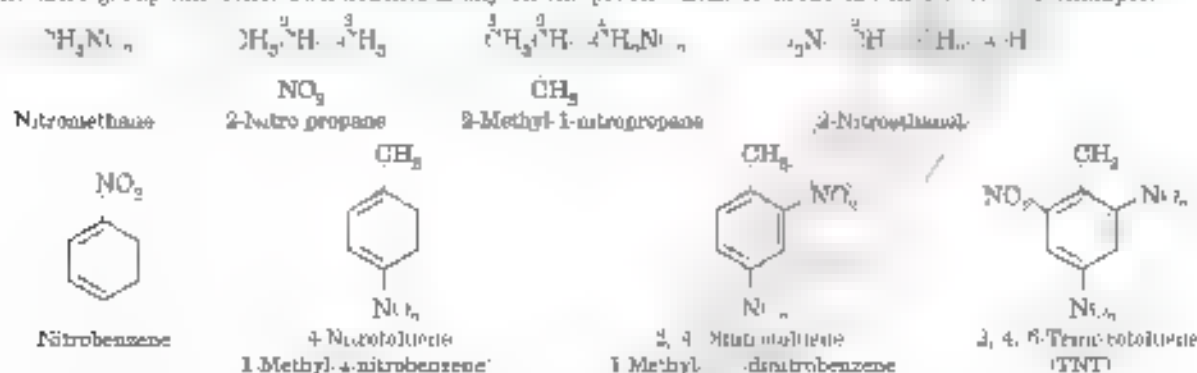
► NITRO COMPOUNDS

These compounds contain the functional group NO_2 . These may be aliphatic or aromatic according as the nitro group is attached to an alkyl or an aryl group.



nitro compound nitro compound

According to IUPAC system, these are named by prefixing **nitro** to the name of parent alkane or arene. The positions of the nitro group and other substituents if any on the parent chain or arene are indicated. For example,

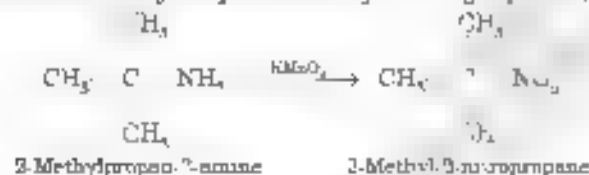


Methods of Preparation of Nitro Compounds

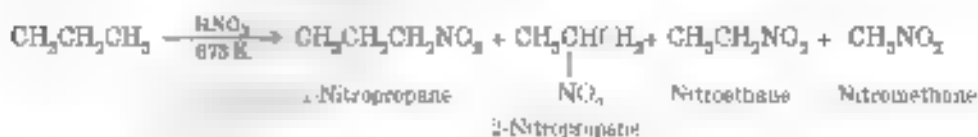
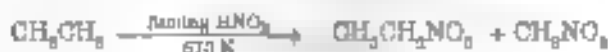
- From alkyl halides by reacting alkyl halide with alcoholic solution of silver nitrate.



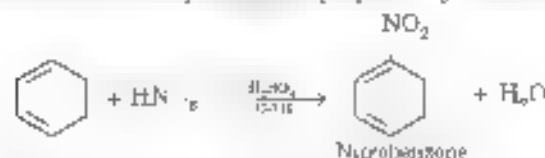
- From tertiary alkyl amines by reacting a primary amine containing a tertiary alkyl group with KMnO_4 oxidation



- From hydrocarbons. With fuming HNO_3 , aliphatic alkanes give a mixture of nitroalkanes resulting by cleavage of carbon-carbon bonds.



Aromatic nitro compounds are prepared by nitration of benzene

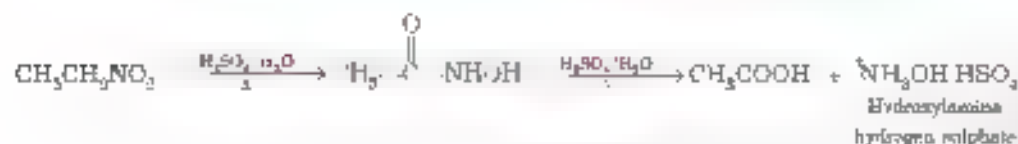


Properties of Nitro Compounds

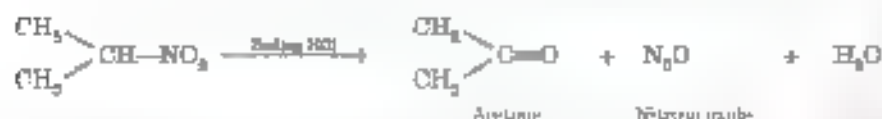
Nitroalkanes are colourless when pure, pleasant smelling liquids. Both nitroalkanes and nitroarenes are highly polar compounds (dipole moment 3.4D) and therefore, have strong dipole-dipole interactions. As a result, nitroalkanes have much higher boiling points than hydrocarbons of comparable molecular masses.

- **Hydrolysis.** Primary nitroalkanes when treated with fuming HCl or 85% H_2SO_4 undergo hydrolysis to form a carboxylic acid and the corresponding salt of hydroxylamine.

Competition File



Secondary nitro compounds upon hydrolysis with boiling H^+ give a ketone and nitrous oxide:



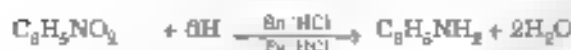
Tertiary nitroalkanes, however, do not undergo hydrolysis with hydrochloric acid.

2. **Reduction.** The nitroalkanes are reduced as:

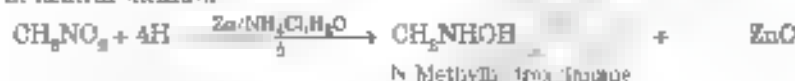


The final product depends upon the pH of the reaction medium and nature of the reducing agent. Some common examples are

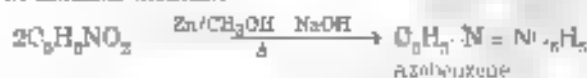
(i) in acidic medium,



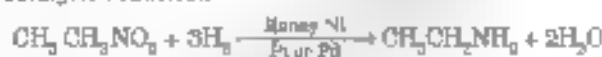
(ii) in neutral medium



(iii) in alkaline medium



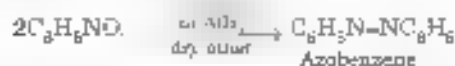
(iv) catalytic reduction



(v) with $LiAlH_4$



Reduction of nitroaromatics give azo compounds

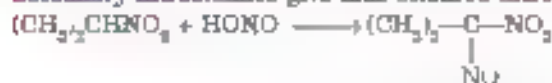


3. **Action with nitrous acid.** Primary nitroalkanes react with nitrous acid $HONO$ to form blue coloured nitroso-nitroalkanes which dissolve in aqueous $NaOH$ to give red solutions.



Competition File

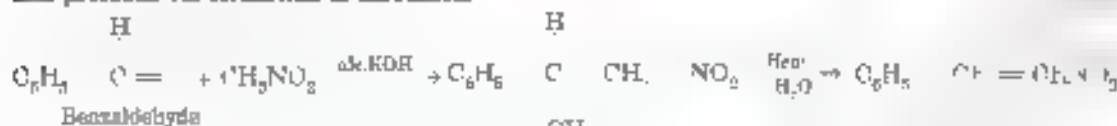
Secondary nitroalkanes give blue coloured nitroso derivative



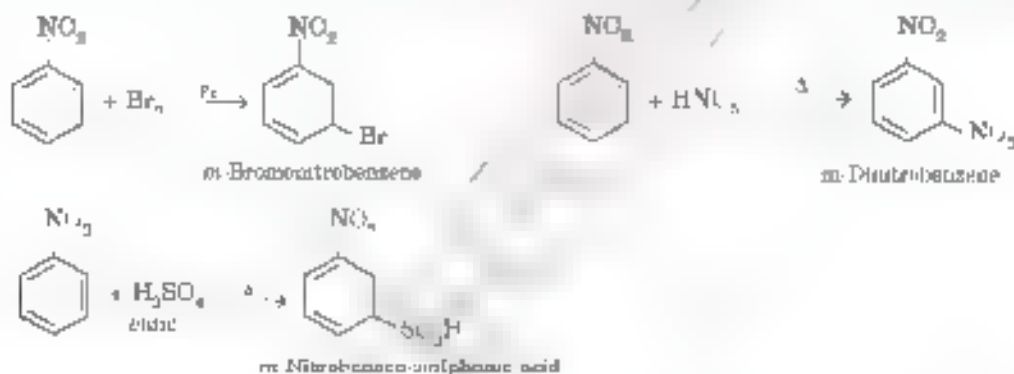
Nitroso derivative (blue)

Tertiary nitroalkanes do not react with nitrous acid because these do not have α -H atoms

4. **Action with aldehydes and ketones.** Due to the presence of α -hydrogen atom primary and secondary nitroalkanes undergo condensation with aldehydes or ketones in the presence of alcoholic KOH. This reaction is quite similar to aldol condensation and proceeds via formation of carbanion.

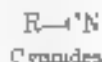


5. **Electrophilic substitution reactions.** Since NO_2 group is strongly deactivating and *m*-directing, therefore, *m*-derivatives are formed.

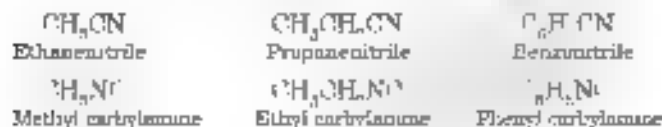


> CYANIDES AND ISOCYANIDES

When the alkyl or aryl group is attached to the carbon of $\text{C}\equiv\text{N}$ group, the compounds are called **cyanides** and when the alkyl or aryl group is attached to the nitrogen atom of $\text{C}\equiv\text{N}$ group, the compounds are called **isocyanides**.

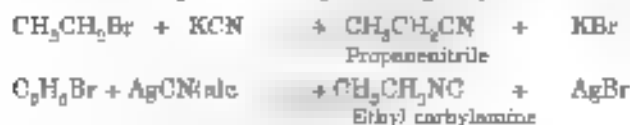


According to IUPAC system, cyanides are called **alkane nitriles** and isocyanides are called **alkyl isocyanides**.

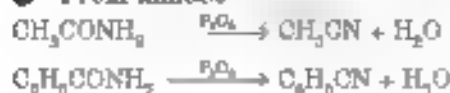


Preparation

- **From alkyl halides** by reacting alkyl halide with KCN or AgCN



- **From amides**



Properties

1. **Hydrolysis.** Alkyl cyanides can be hydrolysed under acidic and basic conditions to give amides, which further get hydrolysed giving carboxylic acids.

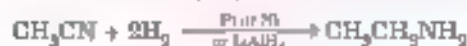


Isocyanides are hydrolysed to primary amines.



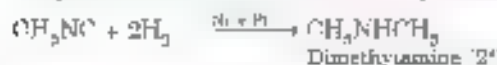
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2. Reduction: Alkyl cyanides are reduced to primary amines either by H_2 in the presence of Ni or Pt or by $LiAlH_4$.

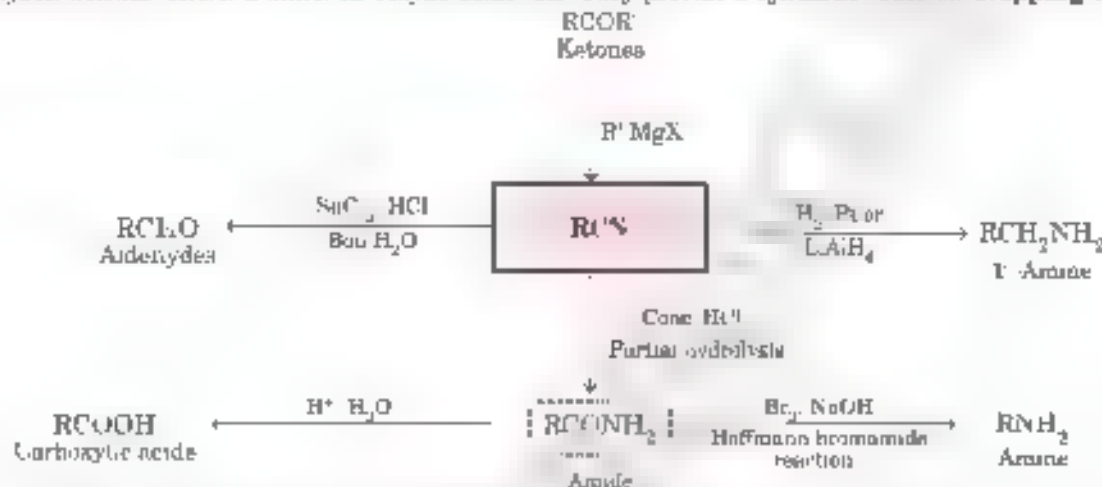


Ethyl amine '1°'

Isocyanides are reduced to secondary amines.



► The alkyl nitriles or cyanides are useful intermediates in organic synthesis because these can be easily converted into amines, aldehydes, ketones, esters, amides, carboxylic acids etc. They provide a synthetic route for **stepping up the series**.



- Acetonitrile (CH_3CN) is used as a solvent of choice for many organic reactions. Its extensive use as solvent is because
- ① It is not reactive in mild acidic and basic conditions.
 - ② It has high polarity and is capable of dissolving a variety of reactants.
 - ③ It has moderate boiling point and therefore, can be easily removed.
 - ④ It is miscible with water and a number of organic solvents.

OBJECTIVE TYPE QUESTIONS

Multiple Choice Questions

M. C. Q.

A (TOPICWISE) MULTIPLE CHOICE QUESTIONS with only one correct answer

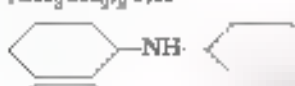

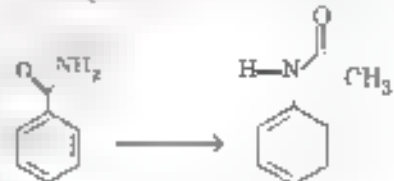
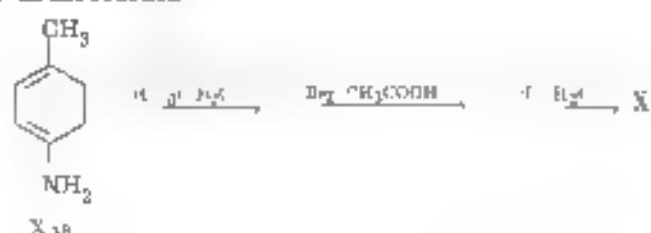
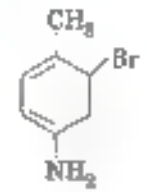
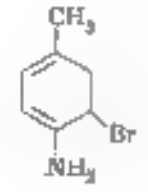
Select the Correct Answer :

Amines

- A1.** Out of the following compounds, which is the most basic in aqueous solution?
- a. CH_3NH_2 b. CH_3NH
c. CH_3NH d. $C_6H_5NH_2$
- A2.** Which of the following amines gives carbylamine reaction?
- (a) $C_2H_5NH_2$ (b) $(C_2H_5)_2NH$
c. $C_6H_5NH_2$ d. $CH_3NHC_6H_5$

- A3.** Aniline undergoes condensation to form Schiff base on reacting with
- a. acetyl chloride b. ammonia
c. acetone d. benzaldehyde
- A4.** An isocyanide on reduction with hydrogen in the presence of Pt gives
- a. amide b. primary amine
c. secondary amine d. alcohol
- A5.** Aniline on oxidation with $Na_2Cr_2O_7$ and H_2SO_4 gives
- a. benzoic acid b. *m*-amino benzoic acid
c. Schiff's base d. *p*-benzoquinone
- A6.** Ethylamine reacts with nitrous acid to form
- a. C_2H_5OH (b) C_2H_5OH, N_2, H_2O
c. $C_2H_5N_2^+Cl^-$ d. $C_2H_5NHCH_2NH_2$

Competition File

- A7.** Hinsberg's reagent is
 (a) benzene sulphonyl chloride
 (b) benzene sulphonie acid
 (c) phenyl isocyanide
 (d) benzene sulphonamide
- A8.** Which of the following reactions is given by only primary amines?
 (a) Reaction with HONO
 (b) Reaction with chloroform and alcoholic KOH
 (c) Reaction with acetyl chloride
 (d) Reaction with Grignard reagent
- A9.** Amino ($-\text{NH}_2$) group is susceptible to oxidation by HNO_3 , therefore, nitration is done in the presence of
 (a) dil. H_2SO_4 (b) CS_2 at 0°C
 (c) CH_3COCl (d) Water
- A10.** Aniline reacts with NaNO_2 and HCl at room temperature to give
 (a) nitroaniline (b) phenol
 (c) diazonium chloride (d) chloroaniline.
- A11.** Silver chloride is soluble in methylamine due to the formation of
 (a) $\text{Ag}^+(\text{CH}_3\text{NH}_2)_2\text{Cl}$ (b) $\text{Ag} + \text{CH}_3\text{Cl} + \text{NH}_4\text{Cl}$
 (c) $[\text{Ag}(\text{CH}_3\text{NH}_2)_2]\text{Cl}$ (d) AgOH
- A12.** Diethylamine reacts with nitrous acid to give
 (a) $(\text{C}_2\text{H}_5)_2\text{NH}^+\text{NO}_2^-$ (b) $\text{C}_2\text{H}_5\text{NO}$
 (c) $\text{C}_2\text{H}_5\text{OH}$ (d) N_2 and alcohol
- A13.** Maximum pK_b value is of
 (a) $(\text{CH}_3)_3\text{NH}$
 (b) $(\text{CH}_3\text{CH}_2)_2\text{NH}$
 (c) 
 (d) 
- A14.** Gabriel phthalimide reaction is used for the preparation of
 (a) primary aromatic amines
 (b) secondary amines
 (c) primary aliphatic amines
 (d) tertiary amines
- A15.** Reaction of ethylamine with chloroform in alcoholic KOH gives
 (a) $\text{C}_6\text{H}_5\text{CN}$ (b) $\text{C}_6\text{H}_5\text{NC}$
 (c) CH_3CN (d) CH_3NC
- A16.** Reaction of acetamide with bromine water and KOH gives
 (a) CH_3COOH (b) $\text{CH}_3\text{CH}_2\text{NH}_2$
 (c) $\text{CH}_3\text{COONH}_2$ (d) CH_3NH_2
- A17.** Hoffmann degradation of *m*-bromobenzamide gives
 (a) aniline (b) *m*-bromoaniline
 (c) bromobenzene (d) *m*-bromoethyl benzene.
- A18.** Which of the following is Hoffmann mustard oil reaction?
 (a) Reaction of aromatic amine with iodoforn
 (b) Reaction of primary amine with CHCl_3
 (c) Reaction of primary amine with CS_2 and HgCl_2
 (d) Reaction of secondary amine with nitrous acid
- A19.** On heating aniline with CS_2 in the presence of HgCl_2 the product is
 (a) Phenyl cyanide
 (b) Phenyl isocyanide
 (c) Phenyl isothiocyanate
 (d) *p*-Aminobenzene sulphonie acid
- A20.** The reagents needed to convert is/are

 (a) KOH , Br_2 , LiAlH_4
 (b) KOH , Br_2 , CH_3COCl
 (c) HONO , CH_3Cl , CH_3COCl
 (d) KOH , Br_2 , Ni , H_2 , CH_3COCl
- A21.** A positive carbylamine test is given by
 (a) *N,N*-dimethylaniline
 (b) 2,4-dimethylaniline
 (c) *N*-methyl-*o*-methylaniline
 (d) *p*-methyl benzylamine
- A22.** In the reaction

 X is
 (a) 
 (b) 

Competition File



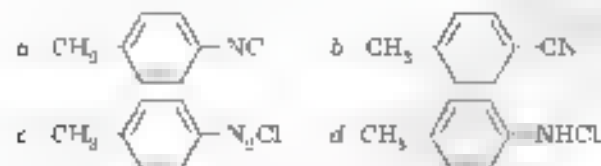
- A23.** The compound $C_6H_{13}N$ is optically active and reacts with $HONO$ to give $C_6H_{11}OH$. The compound is
 (a) *N*-methylbutanamine (b) 2-Aminopentane
 (c) 1-Aminopentane (d) *N,N*-Dimethylpropanamine

- A24.** In the reaction of *p*-chlorotoluene with KNH_3 in liquid NH_3 , the major product is
 (a) *o*-toluidine (b) *m*-toluidine
 (c) *p*-toluidine (d) *p*-chloroaniline

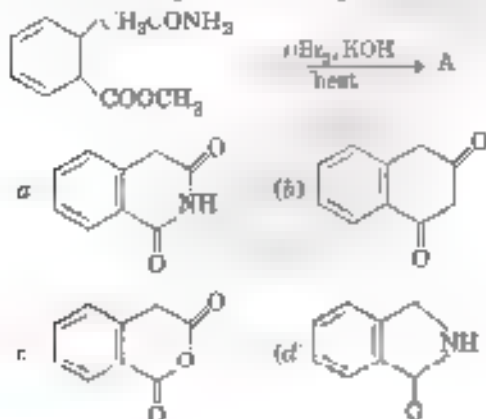
- A25.** *p*-chloroaniline and aluminium hydrochloride cannot be distinguished by
 (a) Sandmeyer's reaction (b) $NaHCO_3$
 (c) $AgNO_3$ (d) Carbylamine test

- A26.** $CH_3CH_2Cl \xrightarrow{NaCN} X \xrightarrow{Ni/H_2} Y \xrightarrow{\text{Acidic hydrolysis}} Z$
 Z in the above sequence is
 (a) $CH_3CH_2CH_2NHCOCH_3$
 (b) $CH_3CH_2CH_2NH_2$
 (c) $CH_3CH_2CH_2CONHCH_3$
 (d) $CH_3CH_2CH_2CONHCOCH_3$

- A27.** The reaction of chloroform with alcoholic KOH and *p*-toluidine forms



- A28.** In the following reaction, the product A is



- A29.** Which of the following compound will dissolve in an alkali solution after it undergoes reaction with Hinsberg's reagent?

- (a) CH_3NH_2 (b) $(CH_3)_2NH$
 (c) $C_6H_5NHC_6H_5$ (d) $(CH_3)_3N$

- A30.** Secondary amines can be prepared by

- (a) reduction of nitriles
 (b) Hoffmann bromamide reaction
 (c) reduction of amides
 (d) reduction of isonitriles

Diazonium Salts

- A31.** Which of the following statement is incorrect?

- (a) Diazonium salts are crystalline solids
 (b) They are unstable and explode in dry state
 (c) Aromatic diazonium salts are less stable than aliphatic diazonium salts
 (d) These are readily soluble in water

- A32.** In Balz-Schiemann reaction, benzene diazonium chloride reacts with

- (a) KI (b) $CuCN/KCN$
 (c) BF_3 (d) BF_3 and $NaNO_2/Cu$

- A33.** The indicator methyl orange is prepared by coupling diazonium salt of sulphanilic acid with

- (a) aniline
 (b) *N,N*-dimethylaniline
 (c) *p*-methylaniline
 (d) naphthol

- A34.** Benzene diazonium chloride on reaction with phenol in weakly basic medium gives

- (a) diphenyl ether (b) *p*-hydroxyaniline
 (c) chlorobenzene (d) benzene

- A35.** Benzene diazonium chloride reacts with nitrous acid in the presence of Cu_2O to give

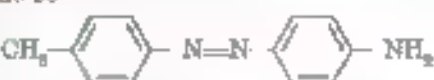

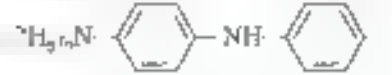

- (a) C_6H_5CN (b) C_6H_5OH
 (c) $C_6H_5NO_2$ (d) C_6H_6

- A36.** Which of the following reaction represents Sandmeyer's reaction?

- (a) $C_6H_5N_2^+Cl^- \xrightarrow{CuCN/KCN} C_6H_5CN + N_2$
 (b) $C_6H_5N_2^+Cl^- \xrightarrow{HCl} C_6H_5Cl + N_2$
 (c) $C_6H_5N_2^+Cl^- \xrightarrow{CuCl/DCl} C_6H_5Cl + N_2$
 (d) $C_6H_5N_2^+Cl^- \xrightarrow{HBF_4} C_6H_5F + N_2$

Competition File

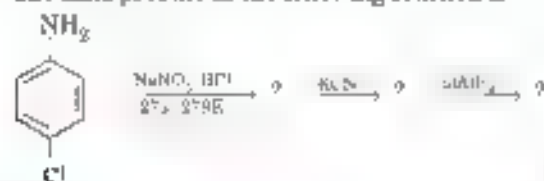
A37. Aniline when diazotized in acid and then treated with dimethyl aniline gives a coloured product. Its structure would be

- a) 
- b) 
- c) 
- d) 

A38. Which of the following diazonium salt is most stable?

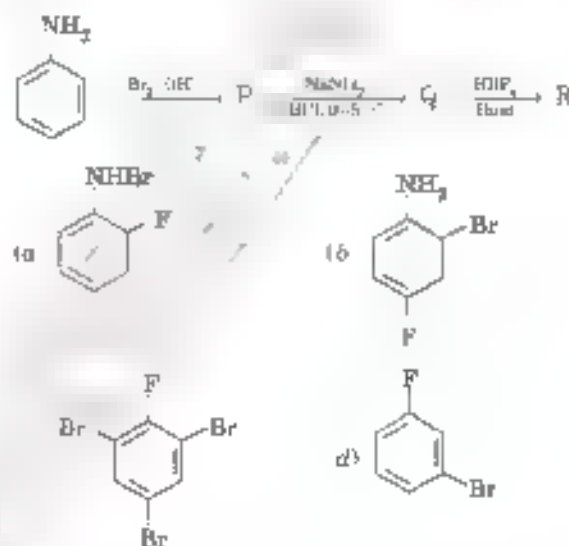
- a) *p*-Nitrobenzenediazonium chloride
 b) 2,4-Dinitrobenzenediazonium chloride
 c) 2,4,6-Trinitrobenzenediazonium chloride
 d) *p*-Methoxybenzenediazonium chloride

A39. The final product in the following reaction is



- (a) *p*-chlorobenzylamine
 (b) *p*-chlorophenol
 (c) *p*-chlorobenzyl alcohol
 (d) *p*-chloro benzamide

A40. The product R in the following reaction is



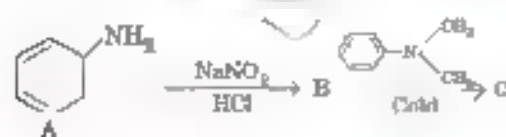
A37. (b) A38. (d) A39. (a) A40. (c)

B (MULTIPLE CHOICE QUESTIONS from competitive examinations AIPMT & Other State Boards' Medical Entrance

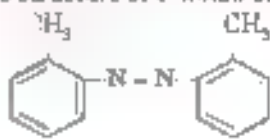
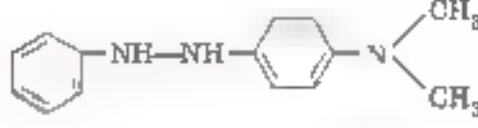
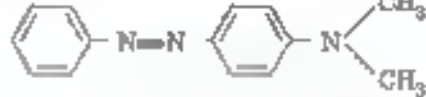
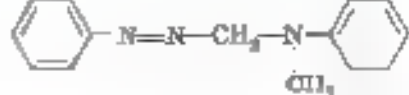
B1. Which one of the following on reduction with lithium aluminium hydride yields a secondary amine?

- a) Methyl isocyanide (b) Acetamide
 c) Methyl cyanide (d) Nitroethane.
 (CBSE Med. 2007)

B2. In a reaction of aniline a coloured product C was obtained.



The structure of C would be

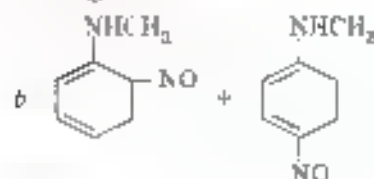
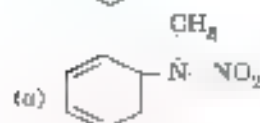
- (a) 
- (b) 
- (c) 
- (d) 

(C.B.S.E. P.M.T. 2008)

B1. a B2. c

Competition File

B3. Predict the product



(C.B.S.E. PMT 2009)

B4. Nitrobenzene can be prepared from benzene by using a mixture of conc. HNO_3 and H_2SO_4 . In the mixture, HNO_3 acts as a/an

- (a) acid (b) base
(c) catalyst (d) reducing agent

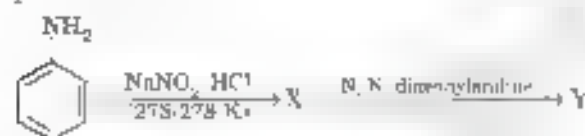
(C.B.S.E. PMT 2009)

B5. Aniline is treated with the following reagents separately. Which one of these would yield methyl aniline?

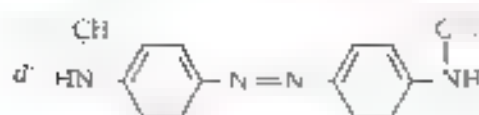
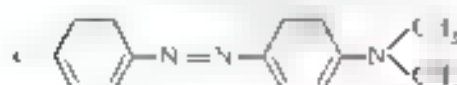
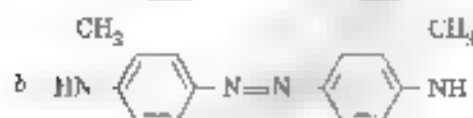
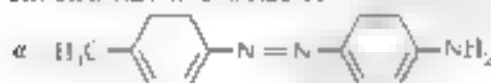
- (a) Hot conc. H_2SO_4 (b) PCl_5
(c) NaOH , Br_2 (d) Soda lime

(C.B.S.E. PMT 2010)

B6. Aniline in a set of the following reactions yielded a coloured product 'Y'



The structure of 'Y' would be



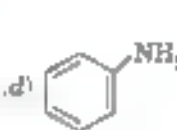
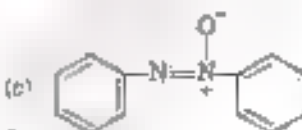
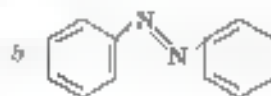
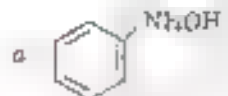
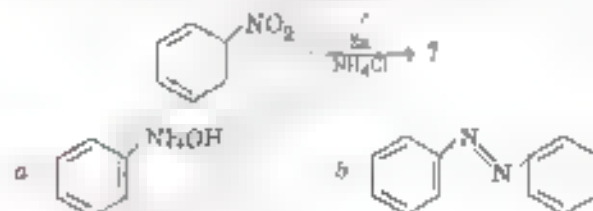
(C.B.S.E. PMT 2010)

B7. Which of the following statements about primary amines is false?

- (a) Aryl amines react with nitrous acid to produce phenols
(b) Alkyl amines are stronger bases than ammonia
(c) Alkyl amines are stronger bases than aryl amines
(d) Aryl amines react with nitrous acid to produce alcohols

(C.B.S.E. PMT 2010)

B8. What is the product obtained in the following reaction?



AIPMT 2011

B9. In the reaction



- (a) H_3PO_4 and H_2O (b) H^+ , H_2O
(c) HgSO_4 , H_2SO_4 (d) Cu_2Cl_2

NEET 2013

B10. Nitrobenzene on reaction with conc. $\text{HNO}_3/\text{H}_2\text{SO}_4$ at $80-100^\circ\text{C}$ forms which one of the following product?

- (a) 1,4-Dinitrobenzene
(b) 1,2,4-Trinitrobenzene
(c) 1,2-Dinitrobenzene
(d) 1,3-Dinitrobenzene

NEET 2015

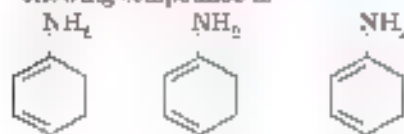
B11. Which of the following will be most stable diazonium salt RN_2^+X^- ?

- (a) $\text{CH}_3\text{N}_2^+\text{X}^-$ (b) $\text{C}_6\text{H}_5\text{N}_2^+\text{X}^-$
(c) $\text{CH}_3\text{CH}_2\text{N}_2^+\text{X}^-$ (d) $\text{O}_2\text{H}_5\text{CH}_2\text{N}_2^+\text{X}^-$

AIPMT 2014, Karnataka CET 2018

Competition File

B21. The correct increasing order of basic strength for the following compounds is



- (a) III < I < II
 (b) III < II < I
 (c) II < I < III
 (d) II < III < I

(NEET 2017)

B32. Nitration of aniline in strongly acidic medium also gives *m*-nitroaniline because

- (a) in spite of substituents, nitro group always goes to only *m*-position
 (b) in electrophilic substitution reactions, amino group is *meta* directive
 (c) in absence of substituents, nitro group always goes to *m*-position
 (d) in acidic (strong) medium, aniline is present as acylium ion.

(NEET 2018)

B33. Aniline is treated with NaNO_2/HCl at 0°C to give compound X which on treatment with cuprous cyanide gives another compound Y. When compound Y is treated with H_2/Ni , compound Z is obtained. The compound Z is

- (a) Benzyl alcohol
 (b) Benzylamine
 (c) N-ethylaniline
 (d) Phenol
 (e) Phenyl hydroxylamine

Kerala PMT 2010

B34. The strongest base in aqueous solution among the following amines is

- (a) N,N-diethylethanamine
 (b) N-ethylethanamine
 (c) N-methylmethanamine
 (d) ethanamine
 (e) phenylmethanamine

Kerala P.M.T. 2011

B25. Aniline is treated with bromine water to give an organic compound 'X' which when treated with NaNO_2 and HCl at 0°C gives a water soluble compound 'Y'. Compound 'Y' on treatment with Cu_2Cl_2 and HCl gives compound 'Z'. Compound 'Z' is

- (a) *o*-bromochlorobenzene
 (b) *p*-bromochlorobenzene
 (c) 2, 4, 6-tribromophenol
 (d) 2, 4, 6-tribromochlorobenzene
 (e) 2, 4-dibromophenol

Kerala P.M.T. 2011

B26. Anilinium hydrogensulphate on heating with sulphuric acid at 453-473 K produces

- (a) benzenesulphonic acid
 (b) anthranic acid
 (c) aniline
 (d) *m*-aminobenzenesulphonic acid
 (e) sulphamic acid

(Kerala P.M.T. 2011)

B27. Secondary amines could be prepared by

- (a) reduction of nitriles
 (b) Hoffmann orthoamide reaction
 (c) reduction of amides
 (d) reduction of isonitriles
 (e) reduction of nitro compounds

Kerala P.M.T. 2015

B28. Which one of the following amines cannot be prepared by Gabriel phthalimide synthesis?

- (a) Ethylamine
 (b) isopropylamine
 (c) *n*-Propylamine
 (d) Ethylmethylaniline
 (e) Allylamine

(Kerala PMT 2015)

B29. Which one of the following amines forms a non-acidic and alkali insoluble product with *p*-toluenesulphonylchloride?

- (a) Tertiary butylamine
 (b) *n*-Butylamine
 (c) Isobutylamine
 (d) Diethylamine
 (e) N,N-Dimethylethylamine

Kerala PMT 2015

B30. Which of the following compound is most basic?

- (a) Aniline
 (b) γ -chloroaniline
 (c) *o*-Nitroaniline
 (d) *o*-Toluidine
 (e) *p*-Methoxyaniline

Kerala PMT 2015

JEE (Main) & Other State Boards' Engineering Entrance

B31. Fluorobenzene can be synthesised in the laboratory

- (a) from aniline by diazotisation followed by heating the diazonium salt with HBF_4
 (b) by direct fluorination of benzene with F_2 gas
 (c) by reacting bromobenzene with NaF solution
 (d) by heating phenol with HF and KF

A.I.E.E.E. 2006

B32. In the chemical reaction,



The compounds A) and B) are respectively

- (a) $\text{CH}_3\text{CH}_2\text{CONH}_2$ and 3KCl
 (b) $\text{C}_6\text{H}_5\text{NC}$ and K_2CO_3
 (c) $\text{C}_6\text{H}_5\text{NO}$ and 3KCl
 (d) $\text{C}_6\text{H}_5\text{CN}$ and 3K^+

A.I.E.E.E. 2007

- B21. (c) B22. (d) B23. (b) B34. (b) B25. (d) B26. (e) B27. (d) B28. (d) B29. (d) B30. (b)
 B31. (a) B32. (c)

Competition File

B43. Choose the amide which on reduction with LiAlH_4 yields a secondary amine

- Ethanamide
- N-Methyl ethanamide
- N, N-dimethyl ethanamide
- Phenyl methanamide
- Butanamide

(Kerala C.E.T. 2009)

B44. Which one of the following is the correct order of increasing basic strength of nitrogen compounds in aqueous solution?

- $\text{NH}_3 < \text{C}_6\text{H}_5\text{NH}_2 < \text{C}_6\text{H}_5\text{NH}_2 < (\text{C}_6\text{H}_5)_2\text{NH} < \text{C}_6\text{H}_5\text{CH}_2\text{NH}_2$
- $\text{C}_6\text{H}_5\text{NH}_2 < \text{NH}_3 < \text{C}_6\text{H}_5\text{CH}_2\text{NH}_2 < \text{C}_6\text{H}_5\text{NH}_2 < (\text{C}_6\text{H}_5)_2\text{NH}$
- $(\text{C}_6\text{H}_5)_2\text{NH} < \text{C}_6\text{H}_5\text{CH}_2\text{NH}_2 < \text{NH}_3 < \text{C}_6\text{H}_5\text{NH}_2 < (\text{C}_6\text{H}_5)_2\text{NH}$
- $\text{C}_6\text{H}_5\text{CH}_2\text{NH}_2 < \text{C}_6\text{H}_5\text{NH}_2 < \text{NH}_3 < \text{C}_6\text{H}_5\text{NH}_2 < \text{C}_6\text{H}_5\text{CH}_2\text{NH}_2$

(Kerala P.E.T. 2012)

B45. Benzylamine is a stronger base than aniline because

- The lone pair of electrons on the nitrogen atom in benzylamine is delocalised.
- The lone pair of electrons on the nitrogen atom in aniline is delocalised.
- The lone pair of electrons on the nitrogen atom in aniline is not involved in resonance.
- Benzylamine has a higher molecular mass than aniline.

(Karnataka C.E.T. 2012)

B46. Which one of the following gives amine on heating with amide?

- Br_2 in aqueous KOH
- Br_2 in alcoholic KOH
- Cl_2 in sodium
- Sodium in ether

(Karnataka C.E.T. 2013)

B47. Positive carbylamine test is shown by

- N, N-dimethylaniline
- triethylamine
- N-methylaniline
- p-methylbenzylamine

(Kerala P.E.T. 2013)

B48. The best reagent for converting 2-phenylpropanamide into 2-phenylpropanamine is

- Br_2 in aqueous NaOH
- excess of H_2
- iodine in the presence of red phosphorus
- LiAlH_4 in ether

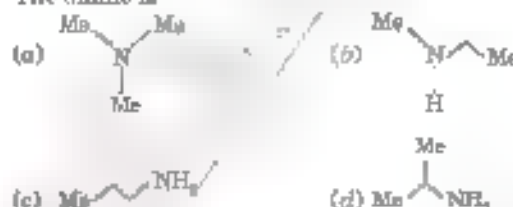
(AMU Engg. 2013)

B49. The reagent with which the following reaction is best accomplished is



- H_3PO_2
- H_3PO_4
- NaHSO_3 (WB JEE 2014)

B50. An amine $\text{C}_3\text{H}_9\text{N}$ reacts with benzene sulphonyl chloride to form a white precipitate which is insoluble in aq. NaOH. The amine is



(WB JEE 2014)

B51. An aromatic compound A ($\text{C}_7\text{H}_9\text{N}$) on reacting with NaNO_2/HCl at 0°C forms benzyl alcohol and nitrogen gas. The number of isomers possible for the compound A is

- 5
- 7
- 8
- 6 (Karnataka C.E.T. 2014)

B52. One of the following amides will not undergo Hoffmann bromamide reaction

- $\text{CH}_3\text{CONHCH}_3$
- $\text{CH}_3\text{CH}_2\text{CONH}_2$
- CH_3CONH_2
- $\text{C}_6\text{H}_5\text{CONH}_2$

(Karnataka C.E.T. 2016)

B53. In the given series of reactions,



The IUPAC name of product Y is

- N-isopropylmethanamine
- N-methylpropan-2-amine
- N-methylpropanamine
- Butan-2-amine (Karnataka C.E.T. 2016)

B54. Diethyl amine when treated with nitrous acid yields

- Diethyl ammonium nitrate
- Ethyl alcohol
- N-nitroso diethyl amine
- Triethyl ammonium nitrate (MH C.E.T. 2015)

B55. The correct order of basicity of the following compounds is



- $1 < 2 < 3 < 4$
- $1 < 2 < 4 < 3$
- $2 < 1 < 3 < 4$
- $4 < 3 < 2 < 1$ (WB JEE 2016)

Answers

- B43. b B44. b B45. b B46. a B47. d B48. d B49. a B50. b B51. a B52. a
B53. b B54. c B55. c

Competition File

B56. Which one of the following can be prepared by Gabriel phthalimide synthesis?

- (a) Aniline (b) o-Toluidine
(c) Benzylamine (d) N-Methylethanamine
(e) 4-Bromoaniline (Kerala PET 2016)

B57. 4-Nitrobenzene is treated with bromine to get compound 'P'. 'P' is reduced with Sn and HCl to get compound 'Q'. 'Q' is diazotised and the product is treated with phosphoric acid to get compound 'R'. 'R' is oxidized with alkaline KMnO_4 to get compound 'S'. Compound 'S' is

- (a) 2-bromo-4-hydroxybenzoic acid
(b) benzoic acid
(c) 4-bromobenzoic acid
(d) 4-hydroxybenzoic acid
(e) 2-bromobenzoic acid (Kerala PET 2016)

B58. In the following sequence of reactions



The compound A is

- (a) propane nitrile (b) ethane nitrile
(c) nitromethane (d) methyl isocyanate

(Karnataka CET 2016)

B59. An organic compound A on reduction gives compound B, which on reaction with trichloromethane and caustic potash forms C. The compound 'C' on catalytic reduction gives N-methyl benzenamine. The compound A is

- (a) nitrobenzene (b) nitromethane
(c) methanamine (d) benzenamine

(Karnataka CET 2016)

B60. The compound that would produce a nauseating smell/odour with a hot mixture of chloroform and ethanolic potassium cyanide is

- (a) PhCONH_2 (b) PhNHCH_3
(c) PhNH_2 (d) PhOH (WB JEE 2017)

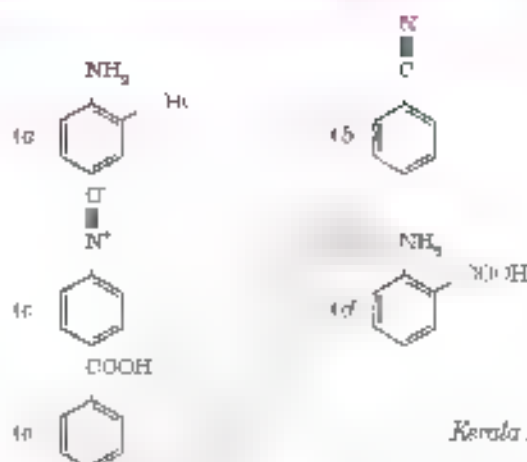
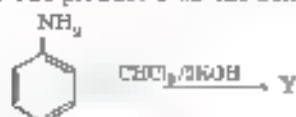
B61. Among Me_3N , $\text{C}_2\text{H}_5\text{N}$ and MeCN (Me = methyl group), the electronegativity of N is in the order

- (a) $\text{MeCN} > \text{C}_2\text{H}_5\text{N} > \text{Me}_3\text{N}$
(b) $\text{C}_2\text{H}_5\text{N} > \text{Me}_3\text{N} > \text{MeCN}$
(c) $\text{Me}_3\text{N} > \text{MeCN} > \text{C}_2\text{H}_5\text{N}$
(d) electronegativity is same in all (WB JEE 2017)

B62. The yield of acetamide in the reaction (100% conversion of 4 moles of aniline with 4 mole of acetic anhydride is

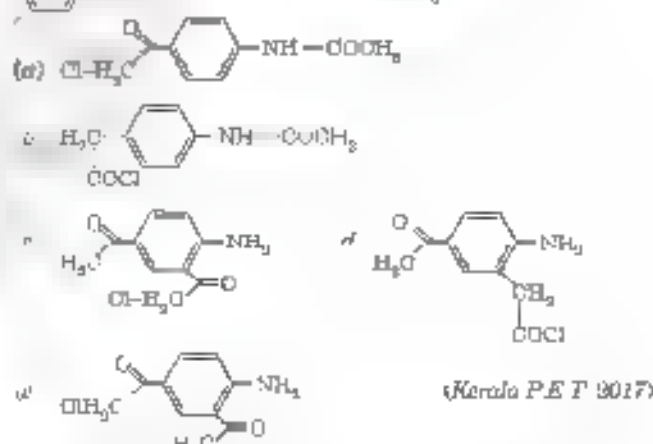
- (a) 274 g (b) 136 g
(c) 67.5 g (d) 177 g (WB JEE 2017)

B63. The product Y for the below reaction is



(Kerala PET 2017)

B64. The product formed in the following reaction is



(Kerala PET 2017)

B65. What product will form when N, N-dimethylaniline reacts with NaNO_2 and dilute HCl at low temperature?

- (a) p-Nitroso-N, N-dimethylaniline
(b) Methyl-n-nerylamine
(c) m-Benzenediazonium chloride
(d) N-Nitroso-N-methylaniline

(JK CET 2018)

B66. Which of the following shows the correct reaction for nitrobenzene reduction?

- (a) Nitrobenzene reacts with Zn dust and NH_4Cl to produce aniline
(b) Nitrobenzene reacts with LiAlH_4 to produce phenyl hydroxylamine
(c) Nitrobenzene reacts with Fe and HCl to produce nitrobenzene
(d) Nitrobenzene reacts with Zn dust and NH_4Cl to produce phenyl hydroxylamine.

(JK CET 2018)

Competition File

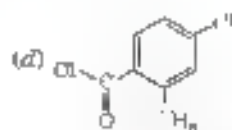
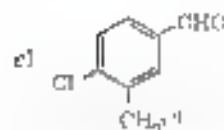
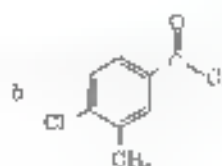
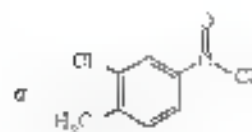
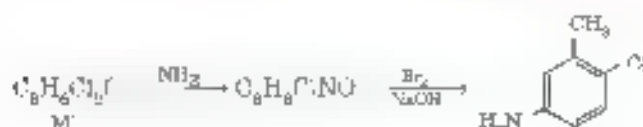
B67. Identify the correct basicity order in the nitroanilines?

(Symbols and notations carry their usual meaning)

- o*-Nitroanilines < *p*-nitroanilines < *m*-nitroanilines
- m*-Nitroanilines < *p*-nitroanilines < *o*-nitroanilines
- p*-Nitroanilines < *o*-nitroanilines < *m*-nitroanilines
- o*-Nitroanilines < *m*-nitroanilines < *p*-nitroanilines

(J K CET 2018)

B68. Identify 'M' in the following sequence of reactions



(WB JEE 2018)

B69. If aniline is treated with conc. H_2SO_4 and heated at 200°C , the product is

- anilinium sulphate
- benzenesulphonic acid
- m*-aminobenzenesulphonic acid
- sulphanilic acid

(WB JEE 2018)

B70. Which of the following is more basic than aniline?

- Diphenylamine
- Triphenylamine
- p*-Nitroaniline
- Benzylamine

(Karnataka CET 2018)

B71. The reaction of acetylsalicylic acid chloride with aniline yields yellow dye. The name of the yellow dye is

- p*-hydroxyazobenzene
- p*-aminazobenzene
- p*-nitroazobenzene
- o*-nitroazobenzene

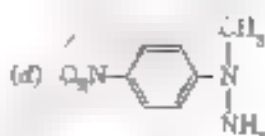
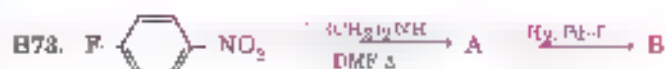
(Karnataka CET 2018)

B72. The nitrosation of *N,N*-dimethylaniline takes place through the attack of electrophile

- nitrosonium ion
- protonated nitrous acid
- nitrous acid
- nitric acid

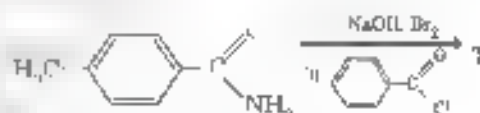
(Kerala PET 2018)

JEE (Advance) for IIT Entrance

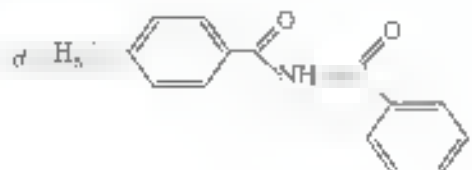
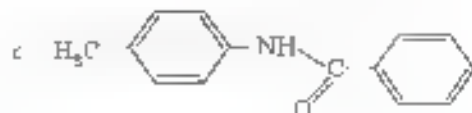
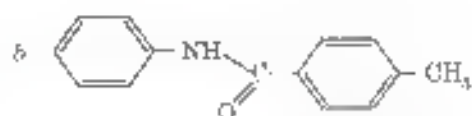
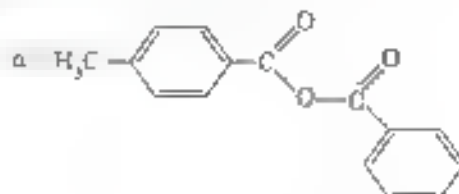


(IIT Screening 2008)

B74. In the reaction



the structure of the product 'T' is

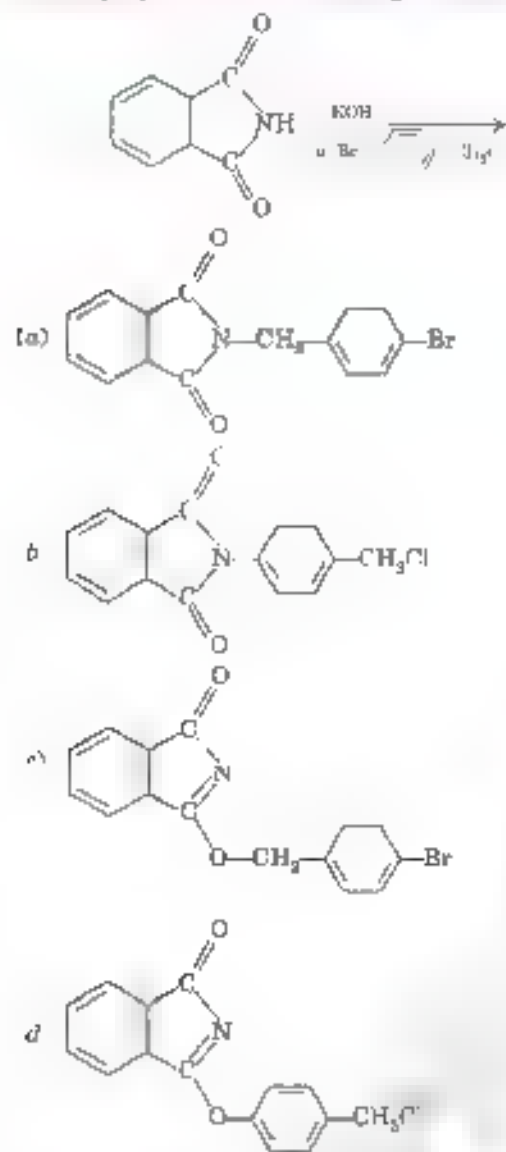


(IIT 2010)

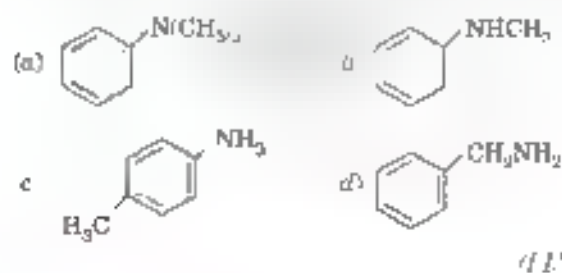
B67. (a) **B68.** (b) **B69.** (d) **B70.** (d) **B71.** (b) **B72.** (a) **B73.** (a) **B74.** (c)

Competition File

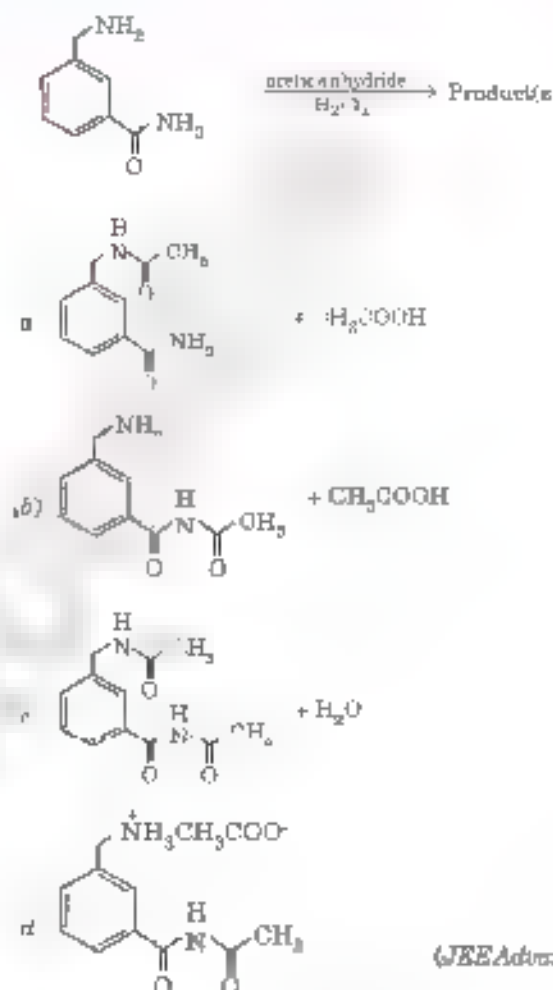
B75. The major product of the following reaction is



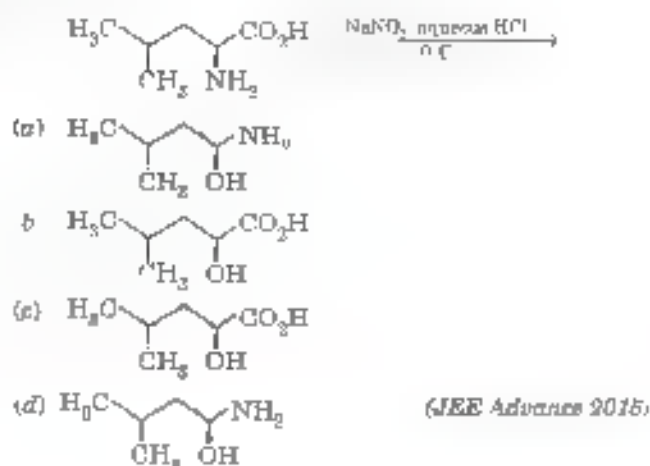
B76. Amongst the compounds given, the one that would form a brilliant coloured dye on treatment with NaNO_2 in dL HCl followed by addition to an alkaline solution of β -naphthol is



B77. In the reaction shown below, the major product(s) formed is/are



B78. The major product of the reaction is

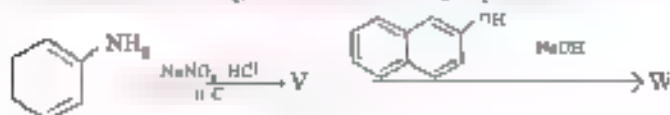


Answers

B75. (c) B76. (c) B77. (d) B78. (c)

Competition File

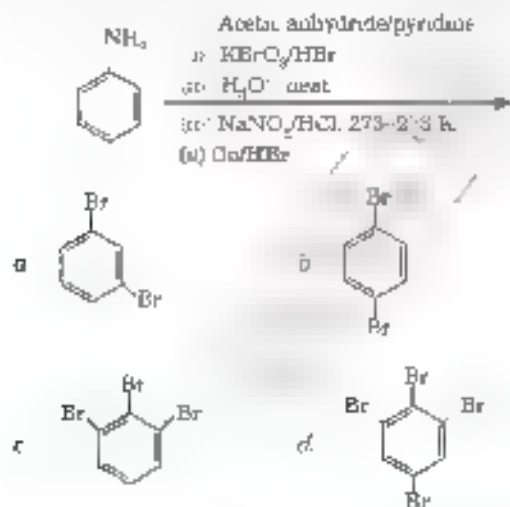
B79. In the following reactions, the major product, W, is



- a)
- b)
- c)
- d)

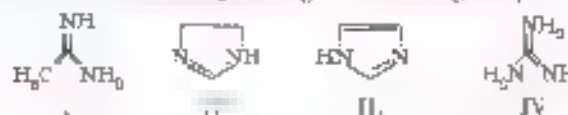
(JEE Advance 2015)

B80. The products of the following reaction sequence are



(JEE Advance 2016)

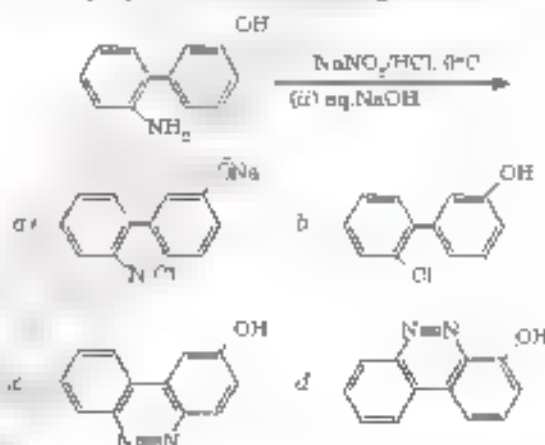
B81. The order of basicity among the following compounds is



- a) $IV > II > III > I$ b) $II > I > IV > III$
 c) $I > IV > III > II$ d) $IV > I > II > III$

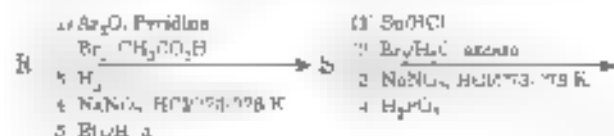
(JEE Advance 2017)

B82. The major product of the following reaction is



(JEE Advance 2017)

B83. Aniline reacts with mixed acid (conc. HNO_3 and conc. H_2SO_4) at 388 K to give P (51%), Q (47%) and R (2%). The major products of the following reaction sequence are



Major products

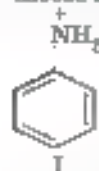
- a)
- b)
- c)
- d)

(JEE Advance 2018)

Competition File

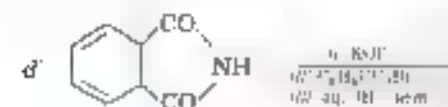
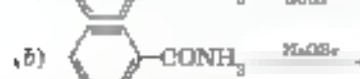
C (MULTIPLE CHOICE QUESTIONS with more than one correct answers

- C1. Examine the following structures for anilinium ion and choose the correct statement from the following



- (a) II is an acceptable canonical structure because carbonium ions are less stable than ammonium ions
 (b) II is not an acceptable canonical structure because it is not aromatic
 (c) II is not acceptable canonical structure because the nitrogen has ten valence electrons
 (d) II is an acceptable canonical structure
- C2. A positive Carbylamine test is given by
 (a) N,N-Dimethylaniline
 (b) 1,4-Dimethylaniline
 (c) N-Methyl-o-methylaniline
 (d) p-Methyl benzylamine

- C3. Which of the following reactions form benzylamine?



- C4. Reaction of RCONH_2 with a mixture of Br_2 and KOH gives RNH_2 as the main product. The intermediates involved in the reaction are

- (a) RCONHBr (b) R-NHBr
 (c) R-N=C=O (d) RCONBr_2

- C5. Which reagents among the following can affect the conversion?



- (a) H_2, Pt (b) Aqueous AgNO_3
 (c) LiAlH_4 (d) NaBH_4

- C6. Which of the following amines undergo acylation reaction?

- (a) $\text{CH}_3\text{CH}_2\text{NH}_2$ (b) $\text{C}_6\text{H}_5\text{NH}_2$
 (c) $(\text{CH}_3)_2\text{CHNH}_2$ (d) $(\text{CH}_3)_3\text{N}$

- C7. In which of the following amines, the first has lower pK_b value than the second?

- (a) Aniline, m-nitro aniline
 (b) Triethylamine, p-toluidine
 (c) Aniline, p-chloroaniline
 (d) Aniline, p-aminophenol

- C8. $2\text{X} + \text{B}_2\text{H}_6 \rightarrow (\text{BH}_2)_2\text{X}_2 + (\text{BH}_4)^-$

The amine X is/are

- (a) NH_3 (b) CH_3NH_2
 (c) $(\text{CH}_3)_2\text{NH}$ (d) $(\text{CH}_3)_3\text{N}$ (IIT 2009)

- C9. The reduction of benzenediazonium chloride to phenylhydrazine can be accomplished by

- (a) $\text{SnCl}_2, \text{HCl}$ (b) Na_2SO_3
 (c) $\text{CH}_3\text{CH}_2\text{OH}$ (d) H_3PO_3 (WB JEE 2017)

- C10. The possible products to be obtained from the reaction of cyclobutyl amine with HNO_2 is/are

- (a) (b)
 (c) (d) $\text{H}_2\text{C}=\text{CH}_2$ (WB JEE 2018)

- C1. (a, c) C3. (b, d) C5. (a, c) C7. (a, c) C9. (a, b, c)
 C2. (a, b) C10. (a, c)

D (MULTIPLE CHOICE QUESTIONS based on the given passage/comprehension

Passage I

Amines are basic in nature due to the presence of lone pair of electrons on N atom of NH_2 group. The basic strength of amines can be expressed by their dissociation constant, K_b or pK_b .



$$K_b = \frac{[\text{RNH}_3^+][\text{OH}^-]}{[\text{RNH}_2]} \quad \text{and} \quad pK_b = -\log K_b$$

Greater the K_b value or smaller the pK_b value, more is the basic strength of amine. Aliphatic amines are stronger bases than ammonia due to the electron releasing effect of alkyl groups. The basic strength among amines decreases as

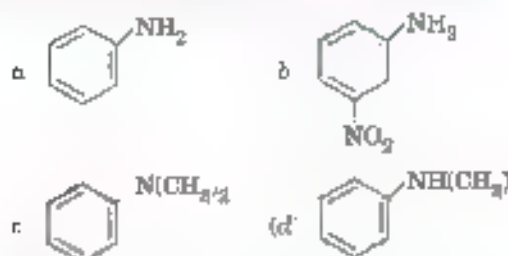
$$2^\circ > 1^\circ > 3^\circ$$

Aryl amines such as aniline are less basic than aliphatic amines due to the involvement of lone pair of electrons on N atom with the resonance in benzenes. In derivatives of aniline, the electron releasing groups increase the basic strength while electron withdrawing groups decrease the basic strength. The basic strengthening effect of electron releasing group and basic weakening effect of electron withdrawing group is more marked at p-position than at m-position. Every o-substituted aniline is less basic than aniline due to ortho effect.

Competition File

Answer the following questions

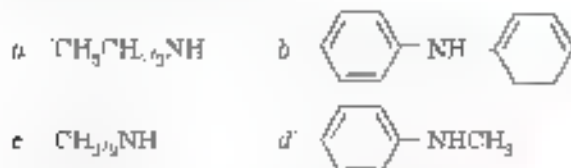
D1. Which of the following has lowest pK_b value ?



D2. Which of the following statement is not correct ?

- a. Ethylamine is more basic than aniline
 b. o-methylaniline has lower pK_b value than aniline
 c. p-methylaniline is less basic than m-methylaniline
 d. Aniline has lower pK_b value than o-nitroaniline

D3. Maximum pK_b value is of



D4. The strongest base among the following is



D5. Which of the following group does not decrease the basic strength of aniline ?



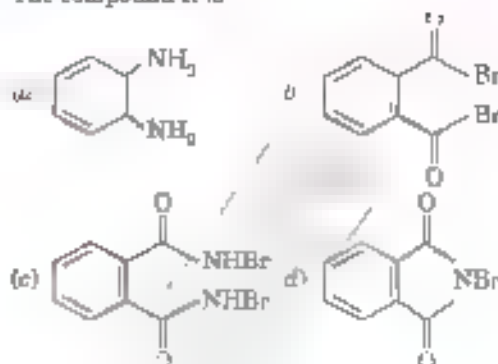
Passage II

Treatment of compound O with KMnO_4/H^+ gave P which on heating with ammonia gave Q. The compound Q on treatment with Br_2/NaOH produced R. On strong heating, Q gave S, which on further treatment with ethyl 2-bromopropionate in the presence of KOH followed by acidification, gave a compound T.



Answer the following questions :

D6. The compound R is



D7. The compound T is

- a. glycine b. alanine
 c. valine d. serine (JEE Advance 2016)

Assertion Reason Type Questions

The questions given below consist of an Assertion and a Reason. Use the following key to choose the appropriate answer.

- (a) If both assertion and reason are CORRECT and reason is the CORRECT explanation of the assertion.
 (b) If both assertion and reason are CORRECT but reason is NOT THE CORRECT explanation of the assertion.
 (c) If assertion is CORRECT but reason is INCORRECT.
 (d) If assertion is INCORRECT but reason is CORRECT.
 (e) If both assertion and reason are INCORRECT.

1. **Assertion.** n-Propylamine has higher boiling point than trimethylamine.

Reason. Among n-propylamine molecules, there is hydrogen bonding but there is no hydrogen bonding in trimethylamine.

2. **Assertion.** Aniline does not undergo Friedel Crafts reaction.
Reason. Friedel Crafts reaction is an electrophilic substitution reaction.

3. **Assertion.** Aniline is a weaker base than ammonia.

Reason. Aniline is resonance stabilized.

4. **Assertion.** Carbylamine reaction involves the reaction between 1° amine and chloroform in the presence of alkali.

Reason. 1. In carbylamine reaction, NH_2 group changes to NC group.

Competition File

5. Assertion: Tertiary amines undergo acylation reaction.

Reason: Tertiary amines have replaceable H atom.

6. Assertion: Amine hydrogen sulphate, on heating forms a mixture of *ortho* and *para* aminesulphonic acids.

Reason : The sulphonic acid group is electron withdrawing group.

7. Assertion: Ammonolysis of alkyl halides involves reaction between alkyl halides and alcoholic ammonia.

Reason : Ammonolysis of alkyl halides mainly produces 2° amines.

8. Assertion: Sulphonic acid has high melting point and is practically insoluble in water.

Reason: Sulphonic acid exists as zwitter ion salt.

9. Assertion: Alkyl cyanides and alkyl isocyanides have much higher boiling points than corresponding alkyl halides.

Reason: Cyanides and isocyanides are much more polar than alkyl halides.

10. Assertion: *p*-nitro aniline is a stronger base than *p*-toluidine.

Reason : The electron withdrawing NO_2 group in *p*-nitroaniline makes it a stronger base.

1. (a) 2. b' 3. b' 4. (a) 5. (a') 6. b) 7. c) 8. (a) 9. (a') 10. a.

Matrix Match Type Questions

Each question contains statements given in two columns which have to be matched. Statements in Column I are labelled as A, B, C and D whereas statements in Column II are labelled as p, q, r and s. Match the entries of Column I with appropriate entries of Column II. Each entry in Column I may have one or more than one correct options from Column II. The answers to these questions have to be appropriately bubbled as illustrated in the following example.

If the correct matches are A-q, A-r, B-p, B-s, C-r, C-s and D-q then the correctly bubbled matrix will look like the following:

	p	q	r	s
A	(p)	(q)	(r)	(s)
B	(p)	(q)	(r)	(s)
C	(p)	(q)	(r)	(s)
D	(p)	(q)	(r)	(s)

1. Match the compounds in Column I with their properties/reactions in Column II.

Column I	Column II
A. $\text{CH}_3\text{CH}_2\text{CH}_2\text{CN}$	p. Reduction with Pd/C/H_2
B. $\text{CH}_3\text{CH}_2\text{CH}_2\text{COCH}_3$	q. Reduction with SnCl_2/HCl
C. $\text{CH}_3\text{CH}_2\text{CH}=\text{CHCH}_2\text{CH}_2\text{H}$	r. Development of foul smell on treatment with KOH and CHCl_3
D. $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2$	s. Reduction with diisobutyl aluminium hydride $[(\text{IBAL})\text{-H}]$
	Alkaline hydrolysis

2. Match the reaction in column-I with product formed in column-II.

Column-I	Column-II
A. Gabriel phthalimide reaction	p. $\text{H}_3\text{CCH}_2\text{NH}_2$
B. Reaction product of 1° amine with alcoholic $\text{K}_2\text{Cr}_2\text{O}_7$ and H^+	q. $\text{C}_6\text{H}_5\text{NH}_2$
C. Reaction product of nitrogen containing compound with LiAlH_4	r. $\text{C}_6\text{H}_5\text{CH}_2\text{NH}_2$
D. Reaction product of 1° amides with Br_2 and KOH	s. $\text{C}_6\text{H}_5\text{NC}$

11.

(1) A p, q, s, r
(2) A p, r

B p, s
B q

C p
C p, r

D r
D p, q, s

Competition File

Integer Type or Numerical Value Type Questions

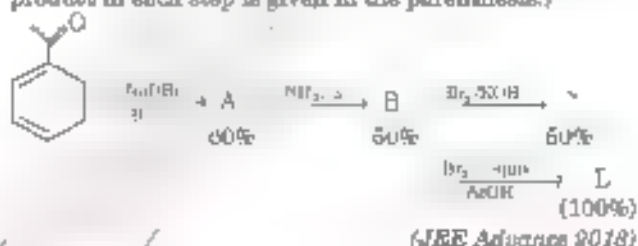
Integer Type: The answer to each of the following question is a **single-digit-integer** ranging from 0 to 9

- The number of isomeric amines corresponding to molecular formula C_6H_5N , which liberates N_2 gas on treatment with nitrous acid is
- The number of amines having pK_b less than $C_6H_5NH_2$ among the following is
 p - $(H_3C)_3C_6H_4NH_2$, o - $(CH_3)_2C_6H_4NH_2$, m - $(CH_3)_2C_6H_4NH_2$, C_6H_5N , CH_3 , $C_6H_5NHCH_3$, p - $NO_2C_6H_4NH_2$, p - $ClC_6H_4NH_2$, H_2N , H_2N , H_2N
- The number of isomeric amines of formula C_7H_9N having a benzene ring is
- The number of isomeric amines of molecular formula C_3H_7N which give carbylamine reaction is

- Total number of nitrogen atoms present in reduced product obtained by reducing nitrobenzene with $LiAlH_4$ followed by aqueous work up is

Numerical Value Type: Give the correct numerical value (in decimal notation truncated/rounded off to the second decimal place)

- In the following reaction sequence, the amount of D (in g) formed from 10 moles of acetophenone is. Atomic weights in $g\ mol^{-1}$: $H = 1$, $C = 12$, $N = 14$, $O = 16$, $Br = 80$ (The yield % corresponding to the product in each step is given in the parenthesis.)



1. 1234567890

1. (2) 2. (5) 3. (5) 4. (8) 5. (3) 6. 405.10



NCERT

Exemplar Problems

Objective Questions

- Which of the following is a 3° amine?
 - 1-methylcyclohexylamine
 - Triethylaniline
 - tert-butylamine
 - N-methylaniline
- The correct IUPAC name for $CH_3-CH(CH_3)-NH_2$ is
 - Aldimethylaniline
 - 2-amino-4-pentene
 - 4-aminopent-1-ene
 - N-methylprop-2-en-1-amine
- Amongst the following the strongest base in aqueous medium is
 - CH_3NH_2
 - $NO_2CH_2NH_2$
 - CH_3NH_2
 - $C_6H_5NHCH_3$
- Which of the following is the weakest Brønsted base?
 - (a)
 - (b)



- Benzylamine may be alkylated as shown in the following equation
 $C_6H_5CH_2NH_2 + R-X \rightarrow C_6H_5CH_2NHR$
 Which of the following alkyl halide is best suited for this reaction through S_N1 mechanism?
 - CH_3Br
 - C_6H_5Br
 - $C_6H_5CH_2Br$
 - C_6H_5Br
- Which of the following reagent would not be a good choice for reducing an aryl nitro compound to an amine?
 - H_2 (excess)/Pt
 - $LiAlH_4$ in ether
 - Fe and HCl
 - Sn and HCl
- In order to prepare a 1° amine from an alkyl halide with simultaneous addition of one CH_3 group in the carbon chain, the reagent used as source of nitrogen is
 - Sodium amide, $NaNH_2$
 - Sodium azide, NaN_3
 - Potassium cyanide, KCN
 - Potassium phthalimide, $C_6H_4(CO)_2N^-K^+$

1. 1234567890

1. (b) 2. (d) 3. (c) 4. (a) 5. (c) 6. (b) 7. (c)

Competition File

8. The source of nitrogen in Gabriel synthesis of amine is

- Sodium azide, NaN_3
- Sodium nitrite, NaNO_2
- Potassium cyanide, KCN
- Potassium phthalimide, $(\text{C}_6\text{H}_4\text{CO})_2\text{N}^-\text{K}^+$

9. Amongst the given set of reactants, the most appropriate for preparing 2° amine is

- 2° $\text{R}-\text{Br} + \text{NH}_3$
- 2° $\text{R}-\text{Br} + \text{NaCN}$ followed by H_2/Pt
- 1° $\text{R}-\text{NH}_2 + \text{RCHO}$ followed by H_2/Pt
- 1° $\text{R}-\text{Br}$ 3 mol, + potassium phthalimide followed by $\text{H}_2\text{O}/\text{heat}$

10. The best reagent for converting 2-phenylpropanamide into 2-phenylpropanone is

- excess H_2
- Br_2 in aqueous NaOH
- Iodine in the presence of red phosphorus
- LiAlH_4 in ether

11. The best reagent for converting 2-phenyl propanamide into 1-phenylethanamine is

- excess H_2/Pt
- NaOH/Br_2
- $\text{NaBH}_4/\text{methanol}$
- $\text{LiAlH}_4/\text{ether}$

12. Hoffmann bromamide degradation reaction is shown by

- ArNH_2
- ArCONH_2
- ArNO_2
- ArCH_2NH_2

13. The correct increasing order of basic strength for the following compounds is



(I)



(II)



(III)

- $\text{I} < \text{II} < \text{III}$
- $\text{II} < \text{I} < \text{III}$
- $\text{III} < \text{II} < \text{I}$
- $\text{II} < \text{I} < \text{III}$

14. Methylamine reacts with HNO_2 to form

- $\text{CH}_3-\text{N}=\text{O}$
- $\text{H}_3\text{C}-\text{N}(\text{O})-\text{CH}_3$
- CH_3OH
- $\text{CH}_3\text{CH}_2\text{OH}$

15. The gas evolved when methylamine reacts with nitrous acid is

- NH_3
- N_2
- H_2
- C_2H_6

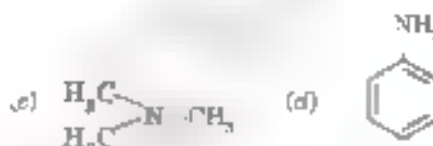
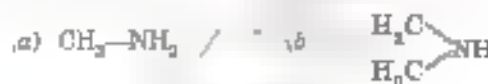
16. In the nitration of benzene using a mixture of conc. H_2SO_4 and conc. HNO_3 , the species which initiates the reaction is

- NO_2
- NO^+
- NO_2^+
- NO_3^-

17. Reduction of aromatic nitro compounds using Fe and HCl gives

- aromatic oxime
- aromatic hydrocarbon
- aromatic primary amine
- aromatic amide

18. The most reactive amine towards dilute hydrochloric acid is



19. Acid anhydrides on reaction with primary amines give

- amide
- amide
- secondary amine
- imine

20. The reaction $\text{ArN}_2^+\text{Cl}^- \xrightarrow{\text{CuHCl}} \text{ArCl} + \text{N}_2 + \text{CuCl}$ is named as

- Sandmeyer reaction
- Cattermann reaction
- Glauber reaction
- Carbylamine reaction

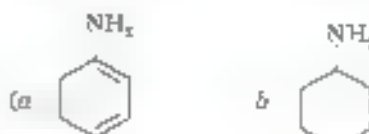
21. Best method for preparing primary amines from alkyl halides without changing the number of carbon atoms in the chain is

- Hoffmann Bromamide reaction
- Gabriel phthalimide synthesis
- Sandmeyer reaction
- Reaction with NH_3

22. Which of the following compound will not undergo azo coupling reaction with benzene diazonium chloride

- Aniline
- Phenol
- Anisole
- Nitrobenzene

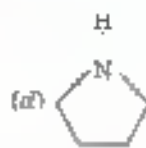
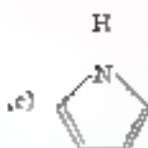
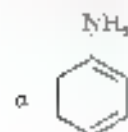
23. Which of the following compounds is the weakest Brønsted base?



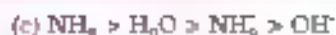
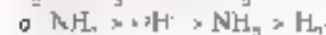
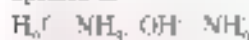
- | | | | | | | | | | | |
|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|
| 8. (d) | 9. (c) | 10. (d) | 11. (b) | 12. (b) | 13. (d) | 14. (c) | 15. (b) | 16. (c) | 17. (c) | 18. (b) |
| 19. (a) | 20. (b) | 21. (b) | 22. (d) | 23. (c) | | | | | | |

Competition File

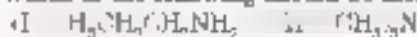
24. Among the following amines, the strongest Brønsted base is



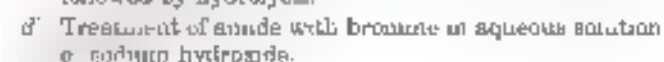
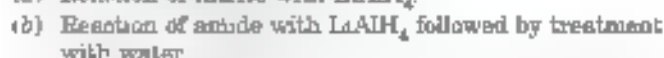
25. The correct decreasing order of basic strength of the following species is



26. Which of the following should be most volatile?



27. Which of the following methods of preparation of amines will give same number of carbon atoms in the chain of amines as in the reactant?



24. d) 25. a 26. b) 27. (c)

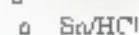
Multiple Choice Questions (Type-B)

Note In the following questions two or more options may be correct.

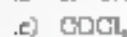
28. Which of the following cannot be prepared by Sandmeyer's reaction?



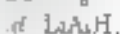
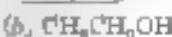
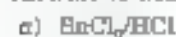
29. Reduction of nitrobenzene by which of the following reagent gives aniline?



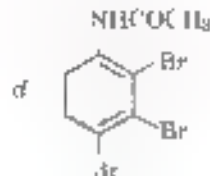
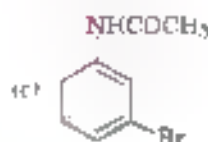
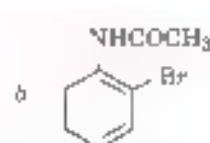
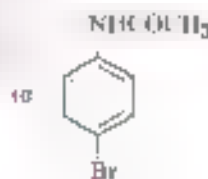
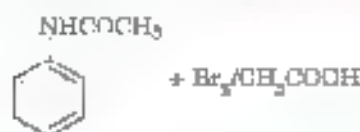
30. Which of the following species are involved in the carbylamine test?



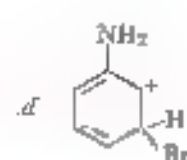
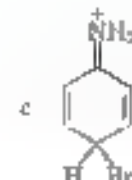
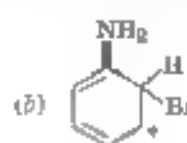
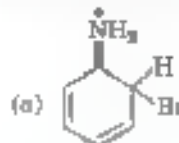
31. The reagents that can be used to convert benzenediazonium chloride to benzene are



32. The product of the following reaction is



33. Aresonium ion involved in the bromination of aniline is



28. c, d

29. a, b, c

30. a, b

31. b, c

32. a, b

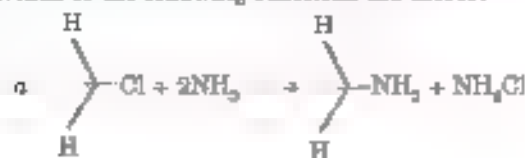
33. a, b, c

Competition File

84. Which of the following amines can be prepared by Gabriel synthesis.

- (a) Isobutyl amine (b) 2-Phenylethylamine
(c) N-methylbenzylamine (d) Aniline

85. Which of the following reactions are correct?



86. Under which of the following reaction conditions, aniline gives *p*-nitro derivative as the major product?

- (a) Acetyl chloride/pyridine followed by reaction with conc. H_2SO_4 + conc. HNO_3
(b) Acetic anhydride/pyridine followed by conc. H_2SO_4 + conc. HNO_3
(c) Dil. HCl followed by reaction with conc. H_2SO_4 + conc. HNO_3
(d) Reaction with conc. HNO_3 + conc. H_2SO_4

87. Which of the following reactions belong to electrophilic aromatic substitution?

- (a) Bromination of acetanilide
(b) Coupling reaction of aryl diazonium salts
(c) Diazotisation of aniline
(d) Acylation of aniline

84. (a), (b)

85. (a), (c)

86. (a), (b)

87. (a), (b)

Matching Type Questions

Note : Match the items of Column I and Column II in the following questions.

88. Match the reactions given in Column I with the statements given in Column II.

Column I	Column II
(a) Ammonolysis	(i) Amine with isocyanide
(b) Gabriel phthalimide synthesis	(ii) Detection test for primary amines
(c) Hoffmann Bromamide reaction	(iii) Reaction of phthalimide with KOH and R-X
(d) Carbylamine reaction with NH_3	(iv) Reaction of alkyl halides

89. Match the compounds given in Column I with the items given in Column II

Column I	Column II
(a) Benzene sulphonyl chloride	(i) Zwitter ion
(b) Sulphathiazole acid	(ii) Hinsberg reagent
(c) Aryl diazonium salts	(iii) Dyes
(d) Aryl diazonium salts	(iv) Conversion to alcohols

88. (a) (iii); (b) (ii); (c) (i); (d) (iv)

89. (a) (ii); (b) (i); (c) (iii); (d) (iv)

Assertion and Reason Type Questions

Note : In the following questions a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices

(a) Both assertion and reason are wrong.

(b) Both assertion and reason are correct statements but reason is not correct explanation of assertion.

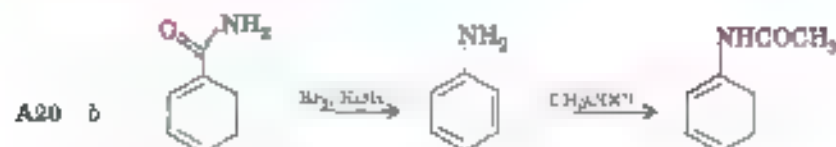
(c) Assertion is correct statement but reason is wrong statement

(d) Both assertion and reason are correct statements and reason is correct explanation of assertion.

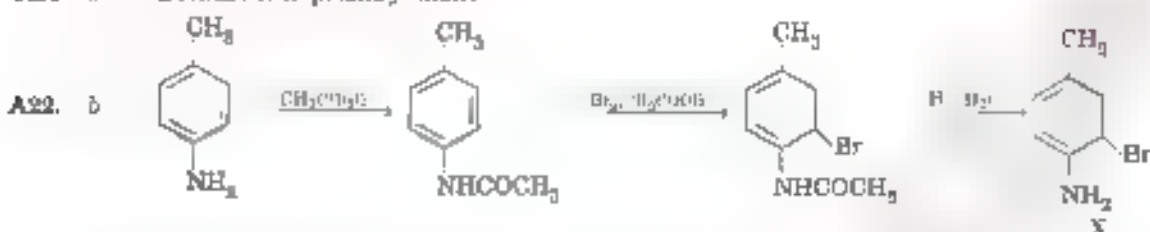
(e) Assertion is wrong statement but reason is correct statement

Competition File

A19. c) Refer A.18. Phenyl isothiocyanate.

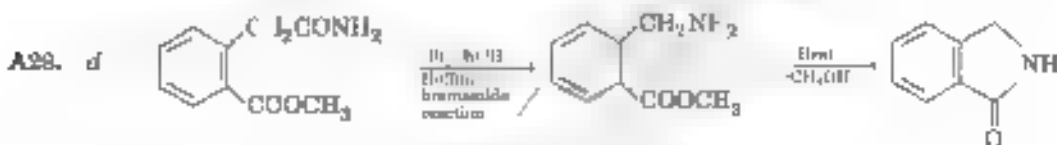


A21. d) Because it is primary amine



A23. b) $\text{CH}_3\text{CH}(\text{NH}_2)\text{CH}_2\text{CH}_2\text{CH}_3$ (2-Aminopentane).

A25. d) Sandmeyer's reaction with chloroaniline gives *p*-dichlorobenzene which is solid m.p. 326 K while that with aniline in chloride gives chlorobenzene which is liquid m.p. 405 K. Ammonium hydrochloride is an acid salt and therefore, liberates CO_2 with NaHCO_3 and gives white ppt. of AgCl with AgNO_3 . However, both are primary amines and give carbylamine test and therefore, cannot be distinguished.

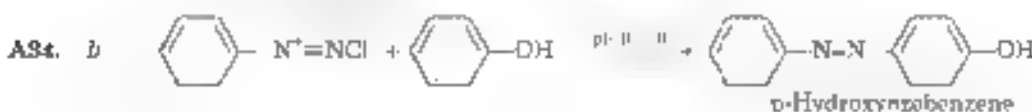


A29. a) Primary amines form benzene sulphonamides which are soluble in alkalis

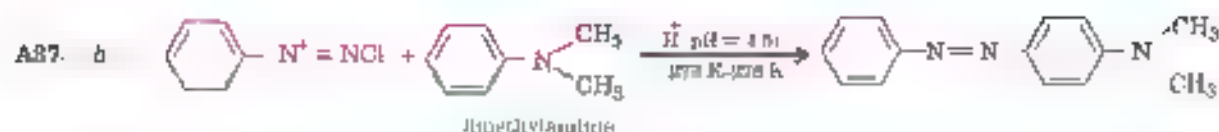
A30. d) i) Secondary amines can be prepared by reduction of isonitriles



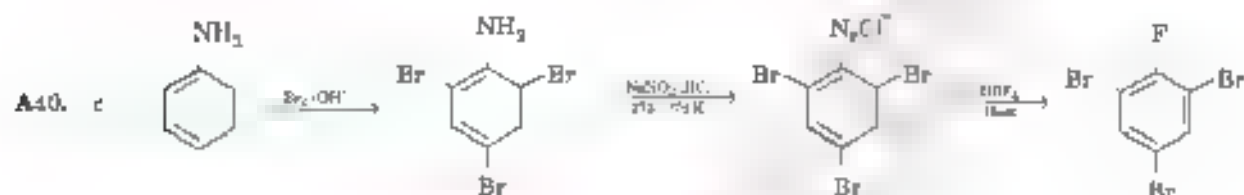
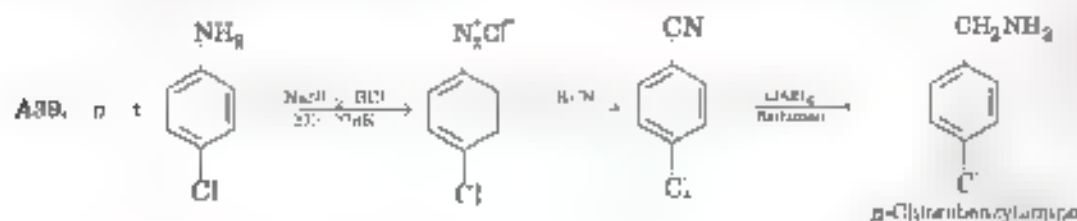
A31. c) Aromatic diazonium salts are more stable than aliphatic diazonium salts because of resonance



Competition File

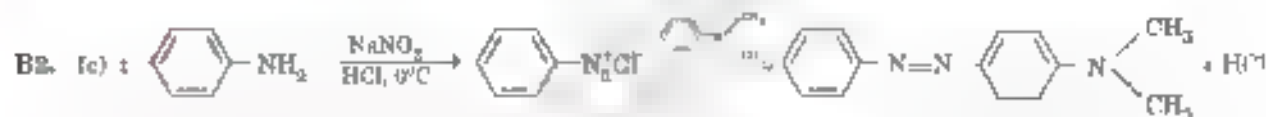


A88. *d* : Electron releasing groups increases the stability of diazonium cations by dispersing the positive charge on the N-atom.



B mcq from Competitive Examinations

B1. *a* : Methylecyanide on reduction with LiAlH_4 gives dimethylamine which is a secondary amine.

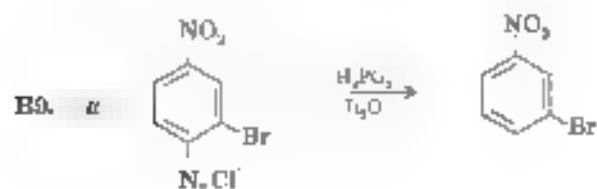
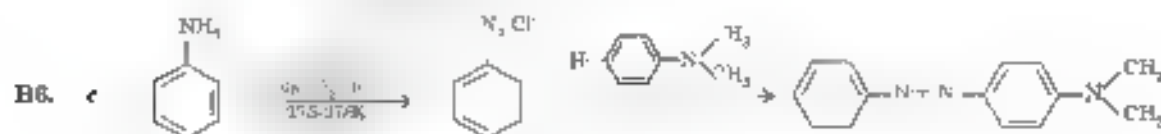


B3. *d* : Secondary aliphatic and aromatic amines react with nitrous acid to form N-nitrosamine.

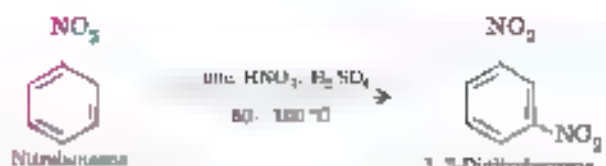

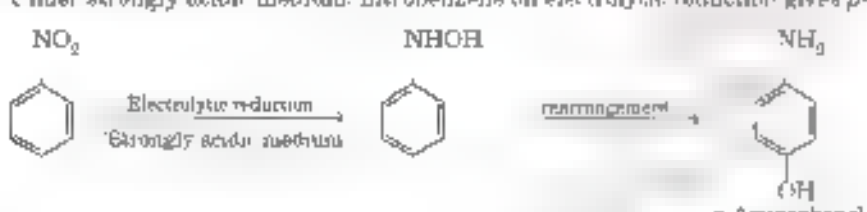
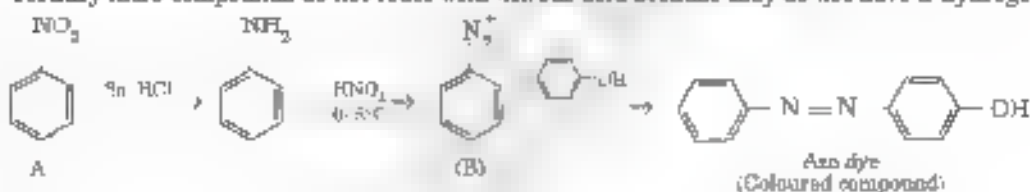
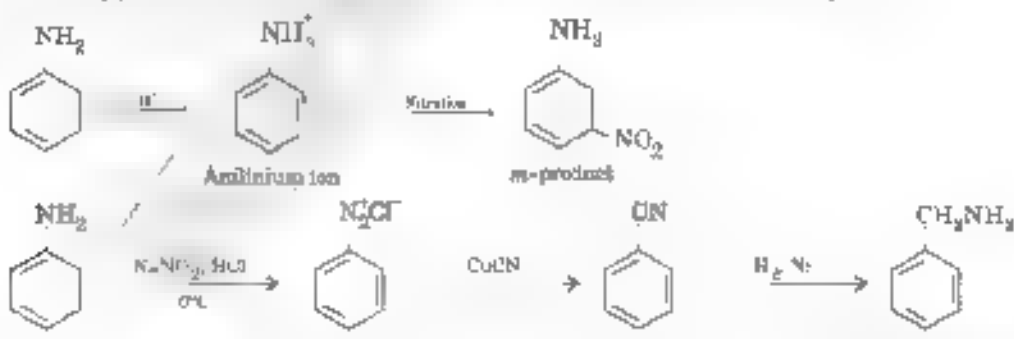
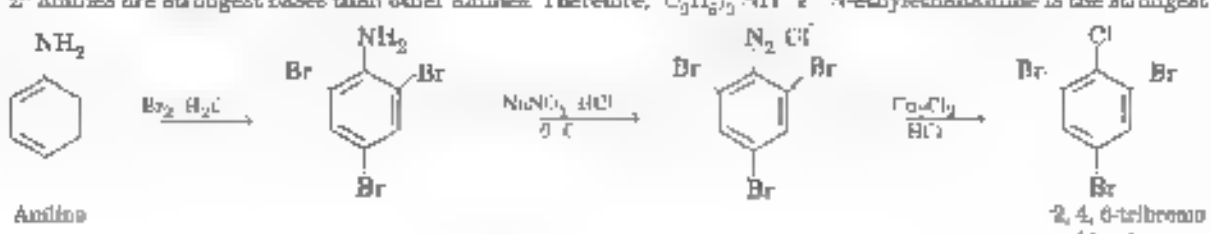
B4. (b) : $\text{HNO}_3 + \text{H}_2\text{SO}_4 \rightarrow \text{NO}_2^+ + \text{H}_2\text{O} + \text{HSO}_4^-$
Here HNO_3 loses OH^- to give NO_2^+ . Hence it acts as a base.



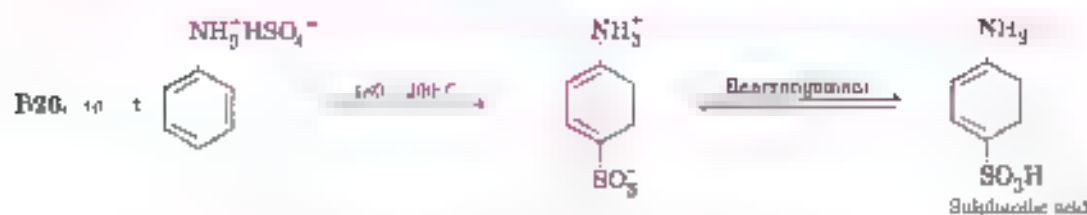
This reaction is Hoffmann degradation reaction.



Competition File

- B10. d**  Nitrobenzene $\xrightarrow[\text{80-100}^\circ\text{C}]{\text{conc. HNO}_3, \text{H}_2\text{SO}_4}$ 1,4-Dinitrobenzene
- B11. b** $\text{C}_6\text{H}_5\text{N}_2^+\text{X}^-$ is most stable diazonium salt because of resonance stabilization
- B12. d** 
- B13. c** Four isomers
 $\text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2$ $\text{CH}_3\text{CH}(\text{CH}_3)\text{NH}_2$ $\text{CH}_3\text{CH}_2\text{NHCH}_2\text{CH}_3$ $\text{CH}_3\text{N}(\text{CH}_3)\text{CH}_2\text{CH}_3$
 Propan-1-amine Propan-2-amine N-Methylethanamine N,N-Dimethylethanamine
- B15. b** Chlorobenzene does not react with potassium phthalimide because aryl halides are less reactive towards nucleophilic substitution reaction.
- B16. c** Under strongly acidic medium, nitrobenzene on electrolytic reduction gives *p*-aminophenol
- 
- B18. (c)** Tertiary amine compounds do not react with nitrous acid because they do not have α -hydrogen.
- B19. b** 
- B20. a** $\text{CH}_3\text{CONH}_2 + \text{Br}_2 + 4\text{KOH} \xrightarrow{\text{Heat}} \text{CH}_3\text{NH}_2 + 2\text{KBr} + \text{K}_2\text{CO}_3 + 3\text{H}_2\text{O}$
 Acetamide Ethylamine
 This is Hoffmann bromide reaction.
- B22. d** In strongly acidic medium, anilinium ion is formed which is meta directing
- 
- B24. b** $\text{C}_2\text{H}_5\text{NH}_2$ is strongest base than other amines. Therefore, $\text{C}_2\text{H}_5\text{NH}_2\text{H}^+\text{Cl}^-$ is the strongest base
- B25. d** 

Competition File



B27. (d) : Secondary amines could be prepared by reduction of isonitriles.

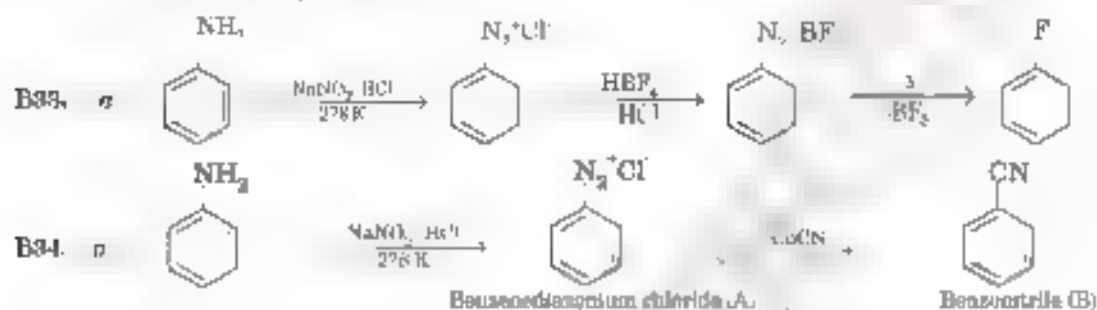


B28. d : Gabriel phthalimide synthesis is used for the preparation of 1° aliphatic amines. Ethylmethylaniline is a 2° amine and hence cannot be prepared by this method.

B29. d : Secondary amines diethylamine give an alkali insoluble product with *p*-toluenealdehyde chloride.

B30. b : Cyclohexyl amine is an aliphatic amine. Aliphatic amines are more basic than aromatic amines.

B32. c : $\text{CH}_3\text{CH}_2\text{NH}_2 + \text{CHCl}_3 + 3\text{KOH} \longrightarrow \text{CH}_3\text{CH}_2\text{NC} + 3\text{KCl} + 3\text{H}_2\text{O}$
This is Carbylamine reaction.



Each $\text{CH}_3-\text{C}(=\text{O})$ group increases the molecular mass by 42

Total increase in molecular mass = $390 - 180 = 210$

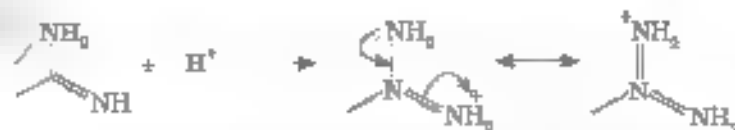
Number of NH_2 groups = $\frac{210}{42} = 5$

B36. b : $\text{CH}_3\text{CH}_2\text{NH}_2$ is most basic and therefore has the smallest pK_b value.

B38. (d) : $\text{RCONH}_2 + 4\text{NaOH} + \text{Br}_2 \longrightarrow \text{RNH}_2 + \text{Na}_2\text{CO}_3 + 2\text{NaBr} + 2\text{H}_2\text{O}$ i.e.
4 mole of NaOH and 1 mole of Br_2 .

B39. c : Aniline is acidic in nature due to protonated to anilinium ion. Anilinium ion is strongly deactivating group and is meta directing. Therefore meta nitration product is obtained in significant amount.

B40. c : The conjugate acid obtained by addition of proton to amine (C) is stabilized by resonance and therefore it is most basic.



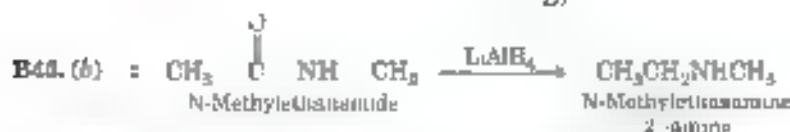
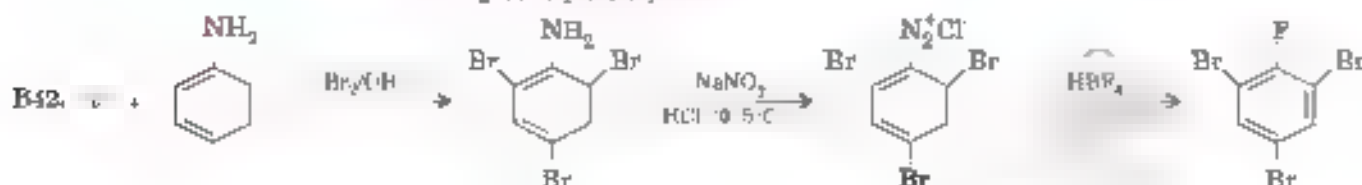
The amine (D) is secondary amine and it is more basic than primary amine (A). The amine (B) is least basic because N atom in it is sp^2 hybridised. Since a sp^2 hybridised N has more s-character, more electronegative than sp^3 hybridised N in amine (A), the N in amine (B) has lesser tendency to donate its electron pair than amine (A). In other words, it is less basic than primary amine (A). Combining these trends, the basicity of four amines increases as

$\text{B} < \text{A} < \text{(D)} < \text{(C)}$

Competition File

- B41. a** The presence of electron withdrawing group like $-NO_2$ at p -position will decrease the basic character so **3** will be least basic. Presence of electron donating group like $-CH_3$ at p -position will increase the basic character and therefore, **4** is the most basic. The order is

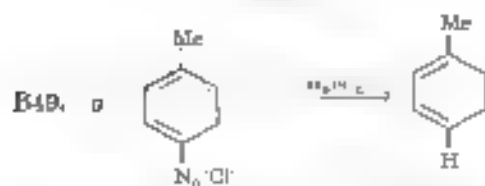
$$2 < 5 < 1 < 3 < 4$$



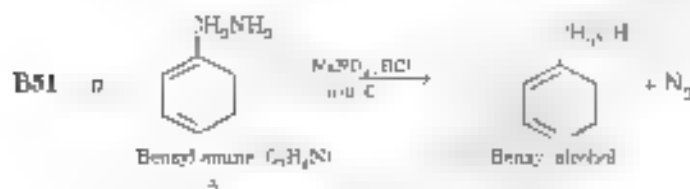
- B46. a** Only treatment of amide with Br_2 in aqueous $NaOH$ or KOH will give amine with lesser number of carbon atoms



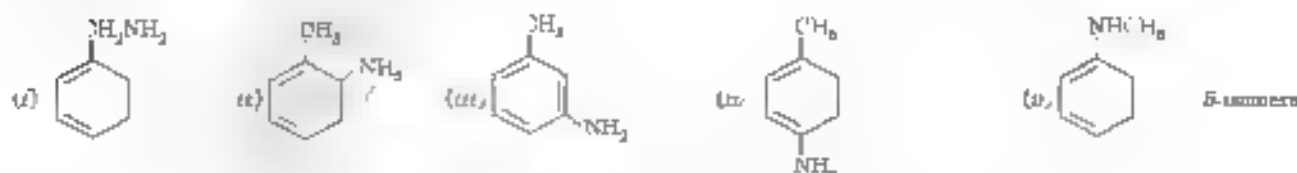
- B47. d'** Primary aliphatic and aromatic primary amines give positive carbylamine test. p -methylbenzylamine is a primary amine and hence gives this test



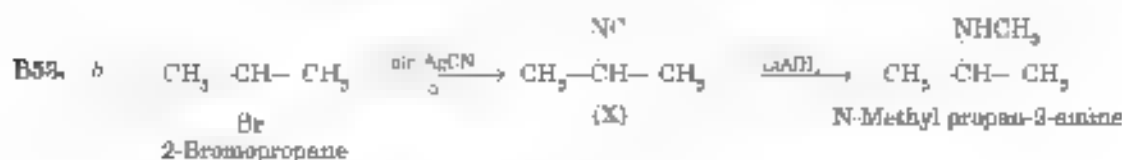
- B50. b** 2° amine reacts with benzene sulphonyl chloride and the product formed is insoluble in $NaOH$. Therefore, the amine should have only one H-atom attached to nitrogen atom.



The possible isomers are



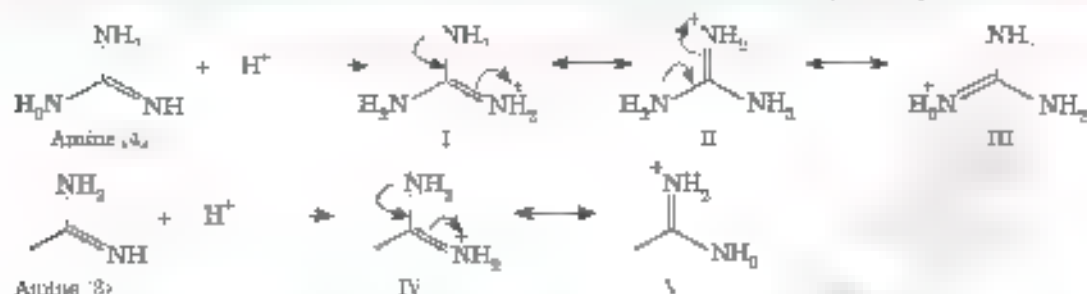
- B52. (a)** Only primary amides undergo Hoffmann bromamide reaction



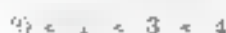
- B54. (c)** $(C_2H_5)_2NH + HONO \rightarrow (C_2H_5)_2N-N=O + H_2O$
N-Nitrosodiethylamine

Competition File

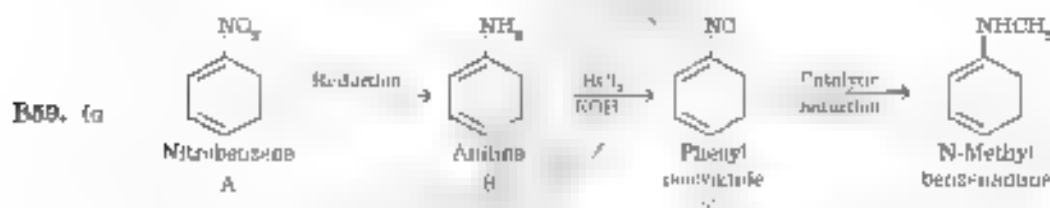
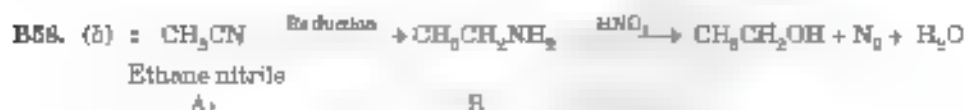
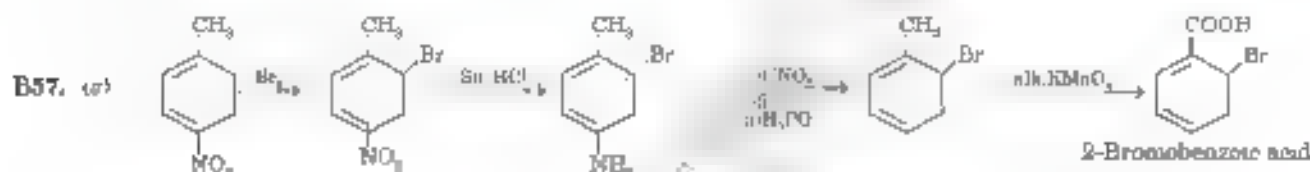
B50. c The conjugate acids obtained by addition of proton to amine 4 is resonance stabilized by three equivalent structures I, II and III while that obtained from amine 5 is resonance stabilized by two equivalent structures IV and V.



Therefore amine 4 is more basic than amine 3. In amine 1, lone pair of electrons is present on a sp^3 hybridized N while in amine 2, it is present on a sp^2 hybridized N. Since a sp^2 hybridized N has more s-character, more electronegative e^- than a sp^3 hybridized N, therefore amine 2 has lesser tendency to form its electron pair than amine 1. In other words, amine 2 is less basic than amine 1. Combining these trends, the hierarchy of four amines increases as:



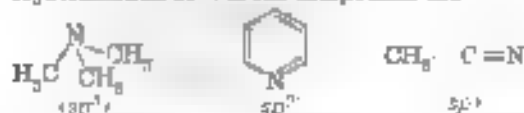
B50. (c) Only primary aliphatic amines can be prepared by Gabriel phthalimide synthesis. Therefore, benzylamine is prepared by this method.



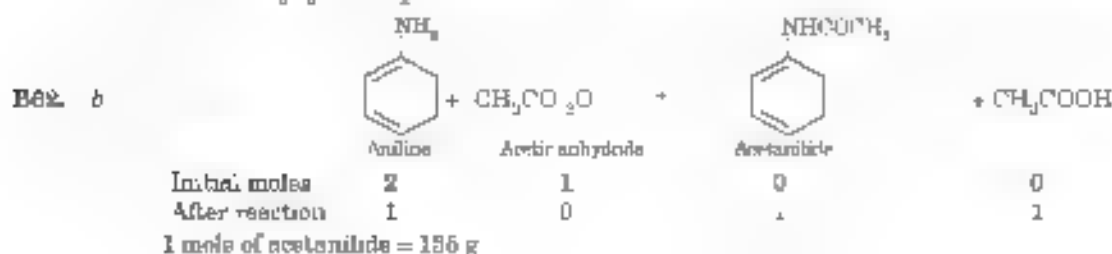
B60. (c) Primary aliphatic and aromatic amines react with CHCl_3 in the presence of alc. KOH and give isocyanides which have nauseating smell/odour.

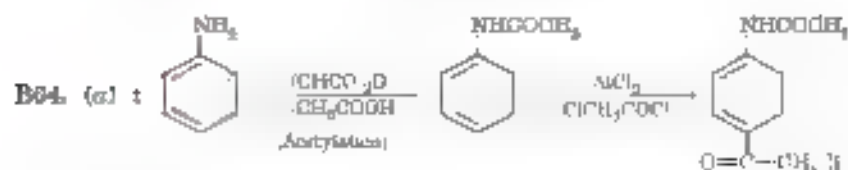


Ed1. σ : Hybridization of N in the compounds are

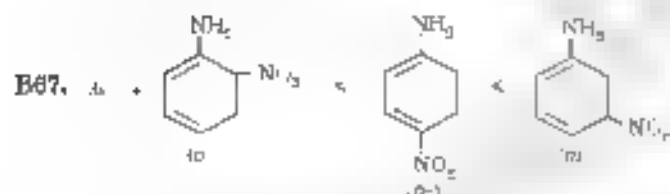
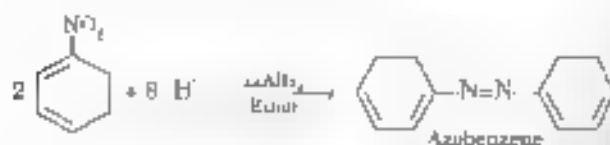
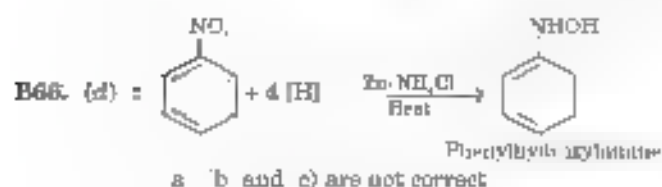
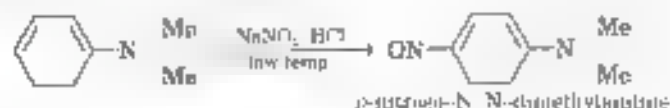


As percentage of s-character increases the electronegativity increases. Therefore, electronegativity order is $\text{MeCN} > \text{C}_2\text{H}_5\text{N} > \text{Me}_3\text{N}$.



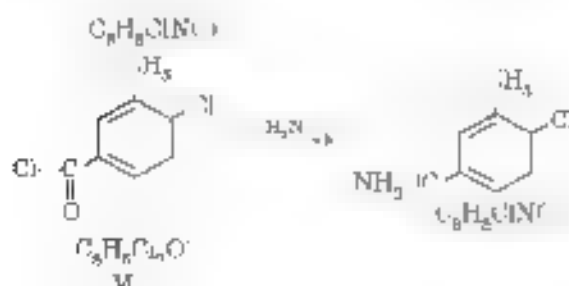
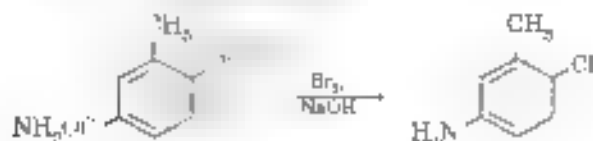


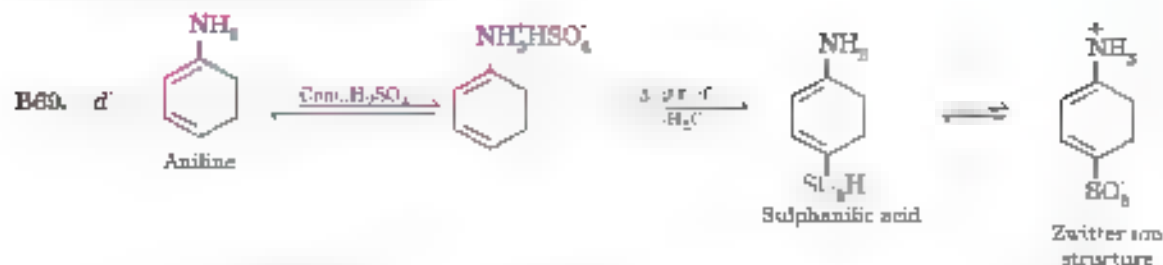
B65. (b) N, N Dimethylaniline 3rd amine forms p-nitroso derivative with HNO_2 .



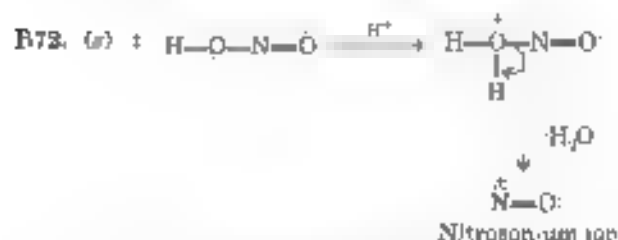
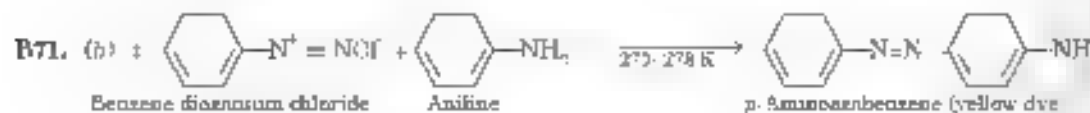
Ortho substituted anilines are weaker bases than others due to ortho effect, which is combination of steric and electronic factors.

B68. (b) Problem can be solved by using back reaction. Hoffmann degradation reaction. Br_2, NaOH converts amides to amines (one carbon atom less).

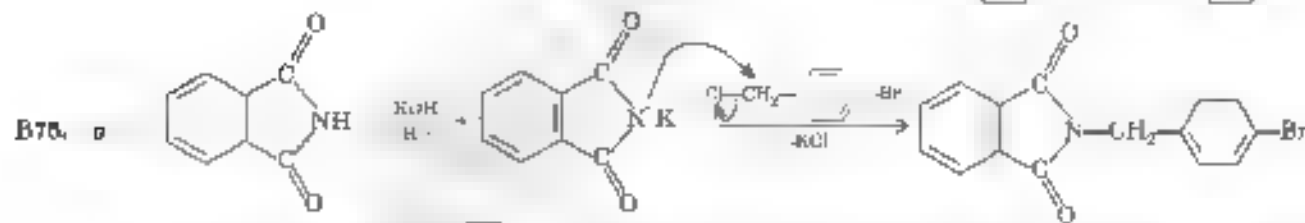
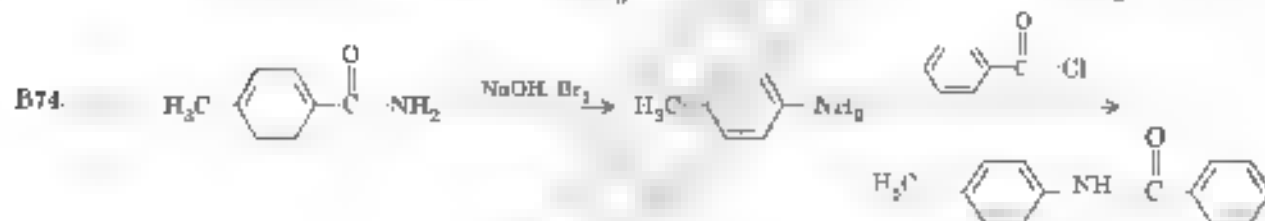




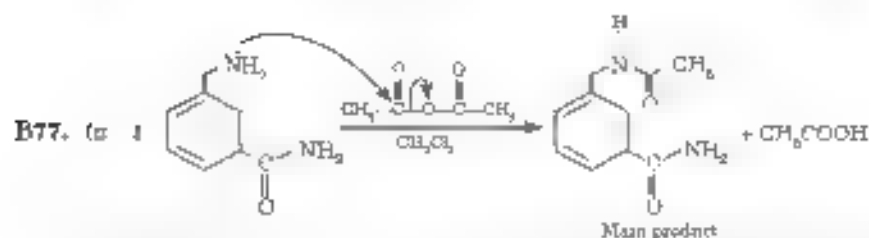
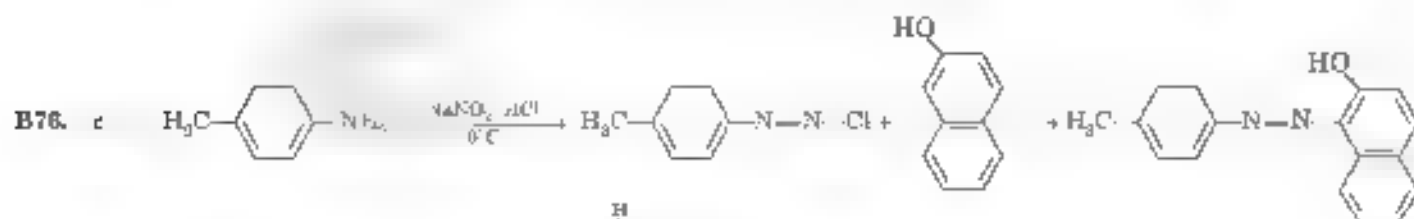
B70. (d) : Benzylamine is most basic among these.



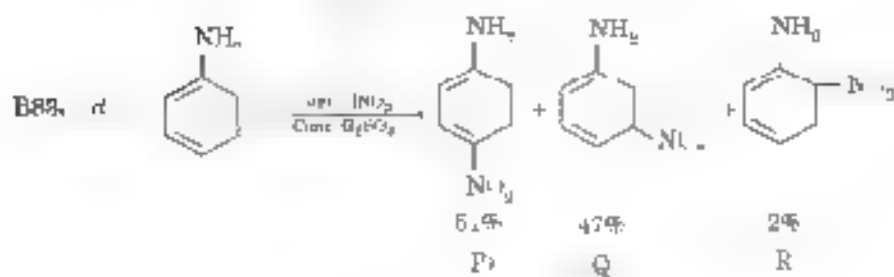
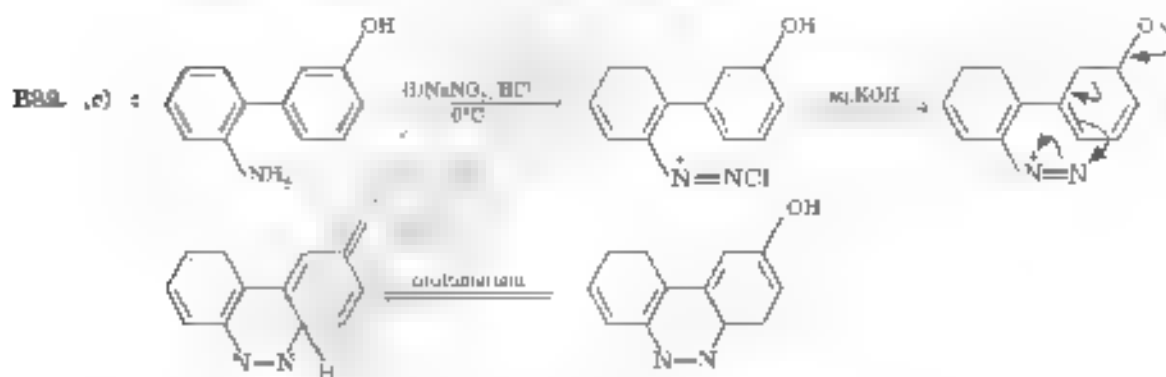
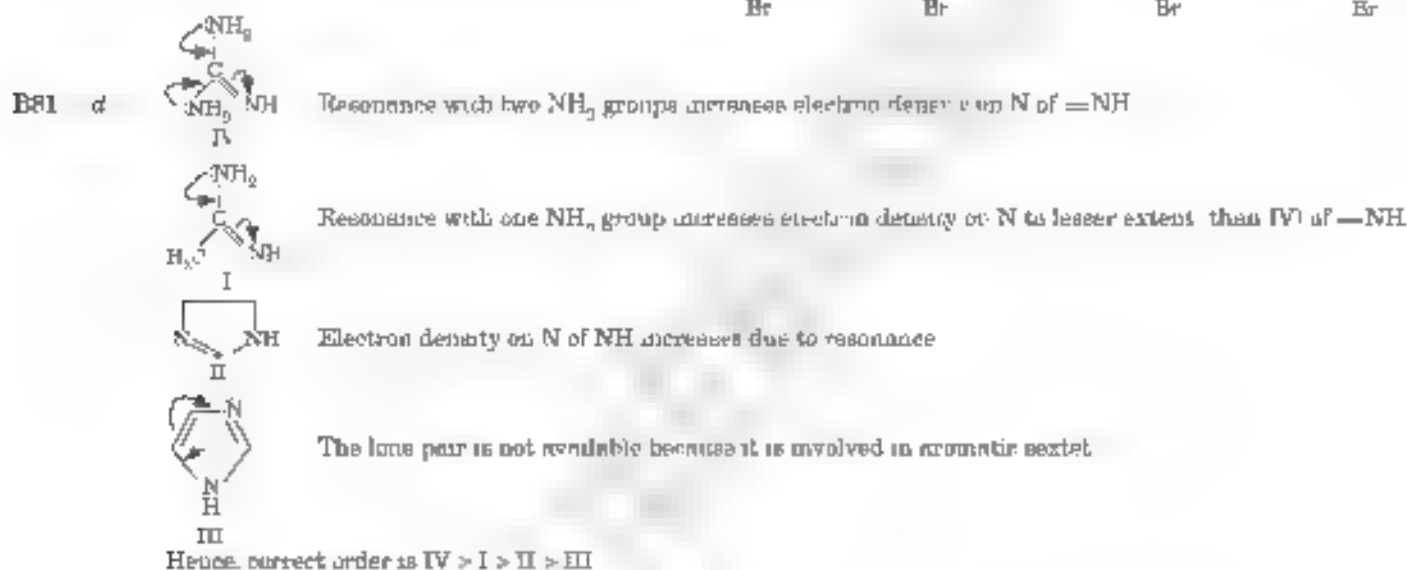
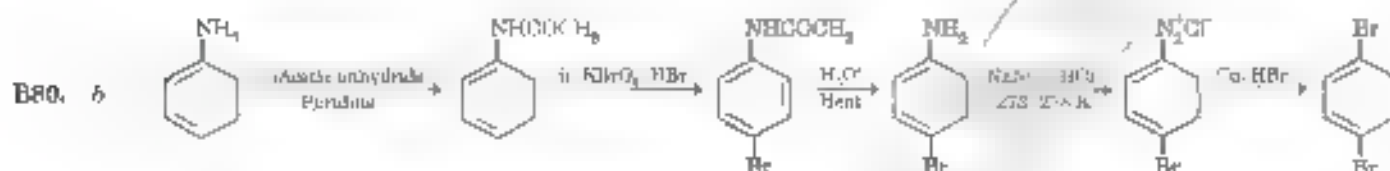
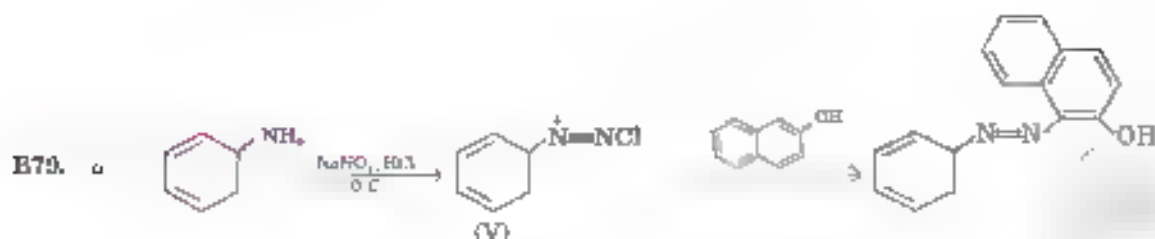
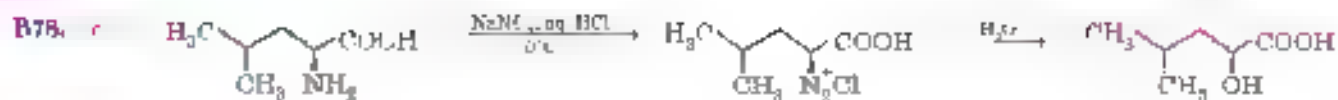
Aromatic tertiary amine i.e. N,N-dimethylaniline undergoes electrophilic substitution with nitrosonium ion at *p*-position of the phenyl ring.

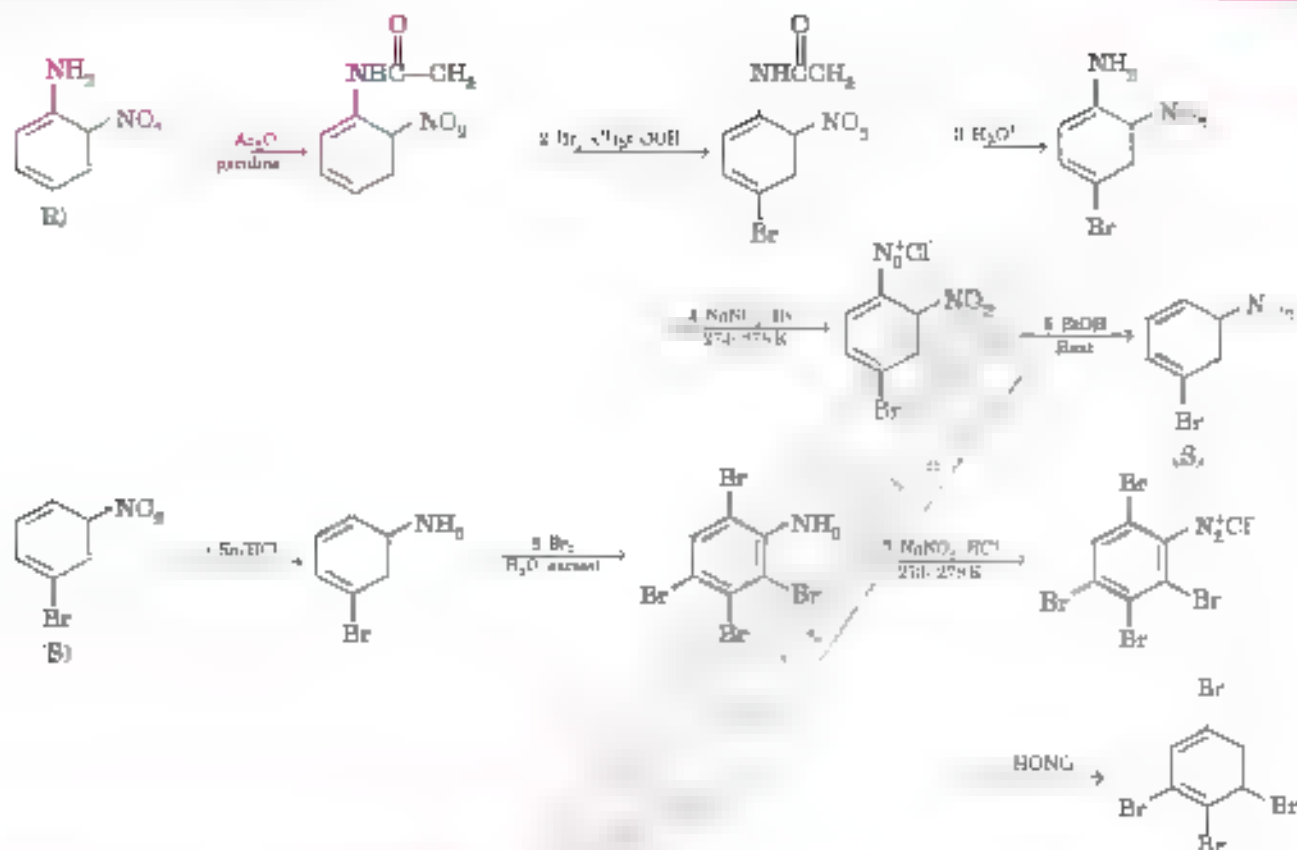


During the attack of $\text{Br}-\text{C}_6\text{H}_4-\text{CH}_2-\text{CH}_2-\text{C}(\text{Br})_2$ C-Br bond is shorter due to resonance and hence is strong. Therefore it cannot take part in the reaction. The Cl takes part in the reaction.



Acetylation takes place when amine or amide reacts with acetyl chloride or acetic anhydride

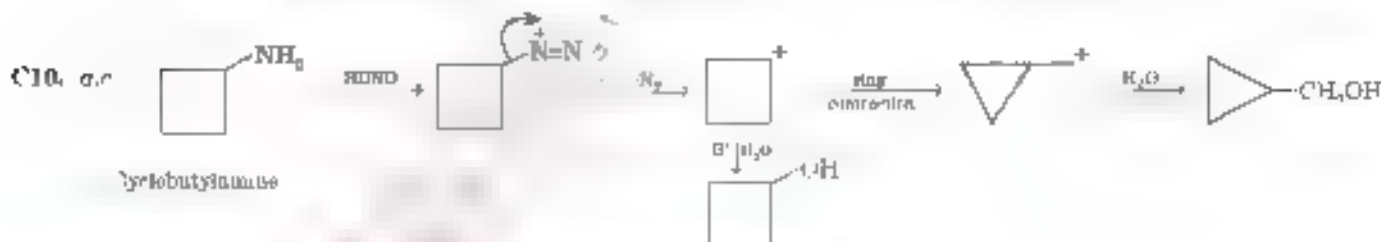




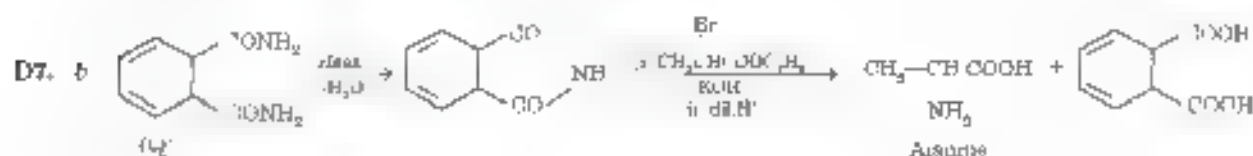
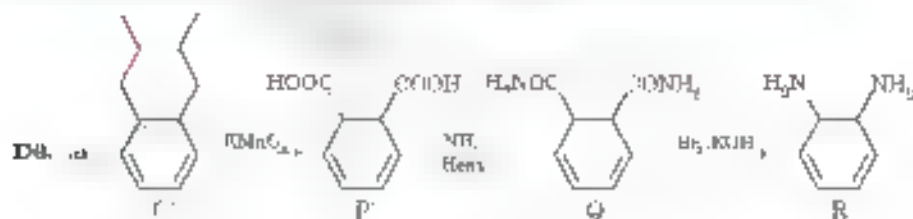
C. mcq with more than one correct answer



Summary: it forms some compounds with 1° and 2° amines. But with 3° amines, it forms adduct.

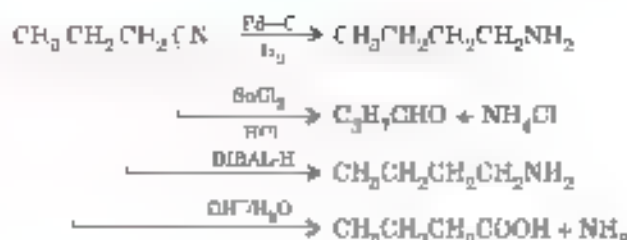


D mcq based on the given passage/comprehension

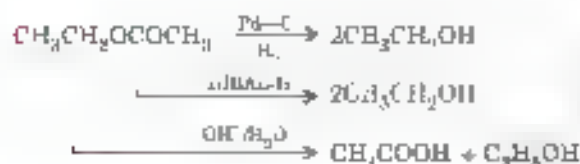


Matrix Match Type Questions

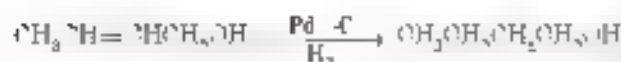
A p q s r



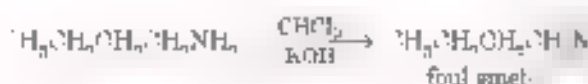
B p r



(C) q

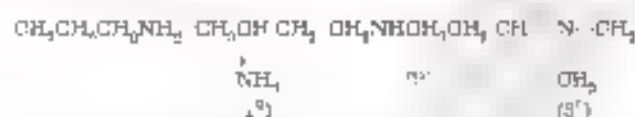
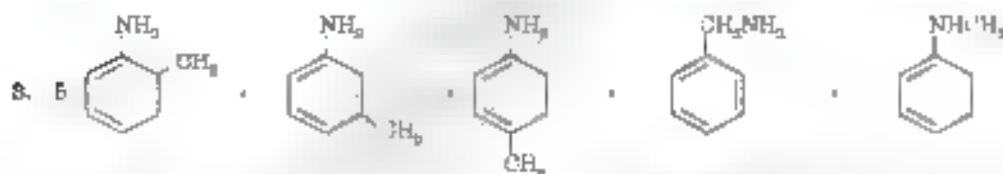
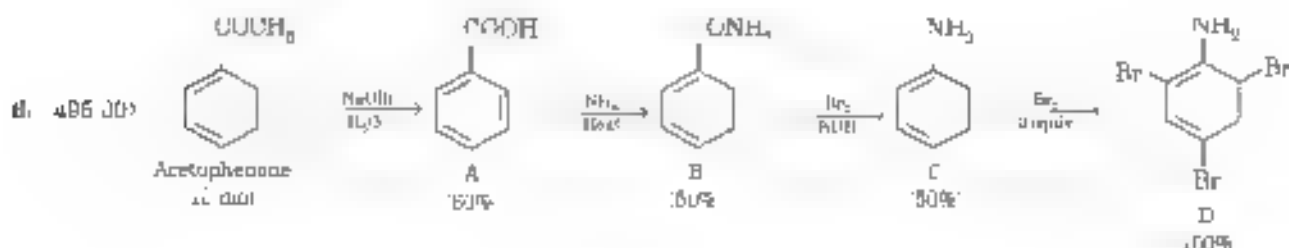
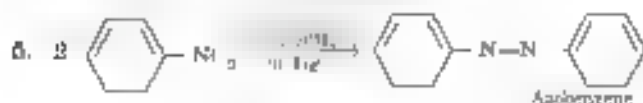


D r



Integer Type or Numerical Value Type Questions

1. (2) Isomeric amines are


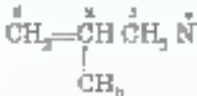
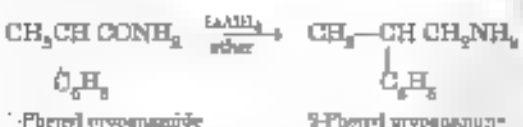

Only primary amine (i.e. A) react with HNO₂ to liberate N₂ gas.2. 5 The amines $p\text{-CH}_3\text{C}_6\text{H}_4\text{NH}_2$, $m\text{-CH}_3\text{C}_6\text{H}_4\text{NH}_2$, $\text{C}_6\text{H}_5\text{N}(\text{CH}_3)_2$, $\text{C}_6\text{H}_5\text{NHCH}_3$, $\text{C}_6\text{H}_5\text{CH}_2\text{NH}_2$ are more basic than aniline and hence have lower pK_a values4. 5 There are eight isomeric amines of molecular formula $\text{C}_6\text{H}_{11}\text{N}$. Out of these only three are primary which give carbylamine reaction

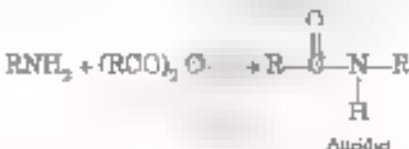
Moles of A formed	=	$\frac{20 \times 60}{100}$	=	0.12 mol
Moles of B formed	=	$\frac{8 \times 50}{100}$	=	0.04 mol
Moles of C formed	=	$\frac{2 \times 50}{100}$	=	0.01 mol
Moles of D formed	=	$\frac{1.5 \times 100}{100}$	=	1.5 mol

Molecular mass of D ($\text{C}_8\text{H}_9\text{Br}_3\text{NH}_2$) = $8 \times 12 + 9 \times 1 + 3 \times 80 + 14 + 2 \times 1 = 330$

Amount of D formed = $330 \times 1.5 = 495.00\text{g}$

NCERT Exemplar Problems : MCQs Type-I

- (b) 
- (a)  N-methylprop-2-en-1-amine
- Due to delocalisation of a lone pair of electrons present on the N-atom into the benzene ring, $\text{C}_6\text{H}_5\text{NH}_2$ is a weak base.
 - (c) because of the stability of $\text{C}_6\text{H}_5\text{CH}_2^+$ carbocation.
 - (d) $\text{C}_6\text{H}_5(\text{CO})_2\text{N}^-\text{K}^+$
 - $$\text{R}-\text{I}=\text{O} + \text{H}_2\text{NR} \xrightarrow[\text{3rd attack}]{\text{Reductive elimination, 2nd attack}} \text{RCH=NR} \xrightarrow{\text{H}_2, \text{Pt}} \text{R}^2\text{H}_2\text{NHR}$$
- (d) 
- 
 - Electron donating group ($-\text{CH}_3$) increases the basicity of amines while electron withdrawing group $-\text{NO}_2$ decreases the basicity.
 - (c) NO_2^+ is an electrophile.

$$\text{HNO}_3 + \text{H}_2\text{SO}_4 \rightarrow \text{NO}_2^+ + \text{HSO}_4^- + \text{H}_2\text{O}$$
 - (b) The amine which is most basic is most reactive, i.e. $(\text{CH}_3)_3\text{NH}$.
- (a) 
- (d) Nitrobenzene does not undergo azo coupling reaction.
- (b) $(\text{CH}_3)_3\text{N}$ i.e. tertiary amine does not form associated molecules.

NCERT Exemplar Problems : MCQs Type-II

- b
 - c
$$\text{C}_6\text{H}_5\text{NO}_2 \xrightarrow{\text{Zn, NH}_4\text{OH}} \text{C}_6\text{H}_5\text{NHOH}$$
 while all other reagents give amine
- (a), (b) Ortho and para products are formed.
- (a), (b) Only primary aliphatic amines are prepared by Gabriel synthesis.

Unit Practice Test

for Board Examination

Time Allowed : 2 Hrs.

Maximum Marks : 56

- Write the IUPAC name of  1
- Arrange the following in order of their basic strength in aqueous solution
aniline, *p*-nitroaniline, *p*-toluidine 1
- How will you convert aniline into chlorobenzene? Give equation. 1
- Why do amines act as nucleophiles? 1
- Aniline dissolves in aqueous HCl. Why? 1
- Explain.
 (i) Why does the reactivity of NH_2 group get reduced in acetanilide?
 (ii) Why does methylamine has lower boiling point than *n*-butane? 2
- Convert the following
 (i) 3-Methylaniline to 3-nitrotoluene
 (ii) Aniline into 1, 3, 5-tribromobenzene. 2
- What is Gabriel phthalimide synthesis? Why aromatic primary amines can't be prepared by this method? 1
- How do aromatic and aliphatic primary amines react with nitrous acid? 2
- Why are aromatic amines weaker bases than aliphatic amines? 1
- How will you convert
 (i) Benzyl chloride to 2-phenylethanamine
 (ii) Aniline to *p*-bromoaniline
 (iii) Benzoic acid to aniline? 3
- Explain the following reactions by giving one example
 (i) Carbylamine reaction
 (ii) Sandmeyer's reaction
 (iii) Bazar-Schiemann reaction 3
- Explain the following
 (a) Ethylamine is soluble in water, whereas aniline is not.
 (b) Although amino group is -I effecting in aromatic electrophilic substitution reactions, ortho-nitration gives a substantial amount of *m*-nitroaniline
 (c) Aniline does not undergo Friedel Crafts reaction. 3
- Convert the following
 (i) 4-Nitrotoluene to 2-bromobenzoic acid
 (ii) *p*-toluidine into 2-bromo-4-methylaniline
 (iii) acetaldehyde to ethylamine. 3
- Starting with aniline using suitable reagents, outline the synthesis of
 (i) *m*-bromochlorobenzene
 (ii) *p*-nitrobenzene
 (iii) 1, 2, 3-tribromobenzene 3
- (a) How does benzene diazonium chloride react with
 (i) phenol
 (ii) aniline
 (b) Describe the method for the identification of primary, secondary and tertiary amines. Also write chemical equations for the reactions involved. 6

► To check your performance see HINTS AND SOLUTIONS TO SOME QUESTIONS at the end of Part II of the book

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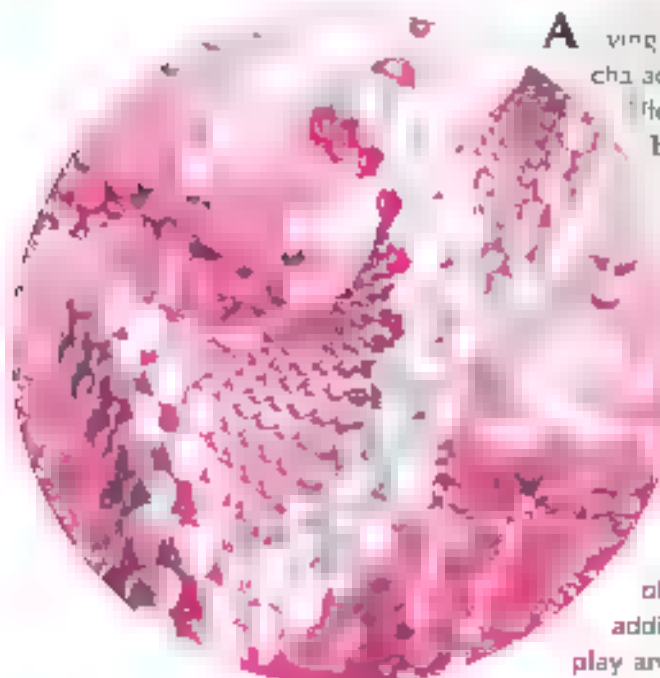
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A living system grows, sustains and reproduces itself. The most amazing characteristic of the living system is that it is composed of several non-living (lifeless) substances which are present in their cells in a very complex but highly organised form. These are called **biomolecules**. Thus, *biomolecules are the complex lifeless molecules which build up living organisms and are required for their growth, maintenance and ability to reproduce. These form the basis of life.* Some common examples are carbohydrates, proteins, enzymes, nucleic acids, lipids, amino acids, fats, etc. These biomolecules interact with each other and constitute the molecular logic of life processes. *The branch of science which deals with the study of biomolecules and their role in living systems is called biochemistry.*

These biomolecules interact with each other in a specific manner to produce life. Many of these biomolecules are polymers. For example, starch, proteins, nucleic acids are condensation polymers of simple sugars, amino acids and nucleotides respectively. In addition, some simple molecules like vitamins and minerals also play an important role in the functions of organisms.

CARBOHYDRATES

Carbohydrates are a class of naturally occurring organic compounds of carbon, hydrogen and oxygen which are primarily produced by plants. These are formed in plants by a process known as *photosynthesis* and make up about 70% of the solid plant material.



- The sugar that we most commonly use is called **sucrose** and
- The sugar present in milk is known as **lactose**.

The common examples are **glucose, fructose, cellulose, sucrose, starch, etc**

In the **earlier days**, the **carbohydrates** were regarded as the **hydrates of carbon** with the general formula $C_xH_xO_{\frac{x}{2}}$. For example, carbohydrates such as glucose $C_6H_{12}O_6$, fructose $C_6H_{12}O_5$, sucrose $C_{12}H_{22}O_{11}$ satisfied this definition. However this definition could not hold good due to the following reasons.

(i). A number of compounds such as rhamnose ($C_6H_{12}O_5$), deoxyribose $C_5H_{10}O_4$, etc. are known which are carbohydrates by their chemical behaviour but do not obey this formula.

(ii). There are other compounds like formaldehyde (CH_2O), acetic acid $C_2H_4O_2$, etc. which do not behave like carbohydrates but have the formula of hydrates of carbon.

(iii). Carbon is not known to form hydrates.

A large number of their reactions have shown that these contain polyhydric aldehydes, polyhydric ketones and large polymeric substances which can be broken down to polyhydric aldehydes or ketones. Therefore, these days **carbohydrates** are defined as

optically active polyhydroxy aldehydes or polyhydroxy ketones or the compounds which produce such compounds on hydrolysis.

Some of the carbohydrates, which are sweet in taste, are also called **sugars**. The most common sugar that we use is called as **sucrose** and sugar present in milk is known as **lactose**. The carbohydrates are also called **saccharides** (Greek *Sakcharon* meaning sugar).

Classification of Carbohydrates

Carbohydrates, in general, may be classified into two classes

(i) **Sugars**. These are crystalline substances which are sweet and water soluble. For example, glucose, fructose and cane sugar.

(ii) **Non-sugars**. These are tasteless, insoluble in water and amorphous. For example, starch, cellulose, etc.

However, these days carbohydrates are **systematically classified** into **three principal classes**

Monosaccharides. These are the simplest carbohydrates which cannot be hydrolysed into simpler compounds. Therefore they represent the simplest single carbohydrate units. About 20 monosaccharides occur naturally. They contain up to six carbon atoms. They have the general formula $C_nH_{2n}O_n$ where $n = 3-7$. The common examples are ribose $C_5H_{10}O_5$, glucose $C_6H_{12}O_6$, fructose $C_6H_{12}O_6$, etc.

(i) **Oligosaccharides**. These are the carbohydrates which give two to ten monosaccharide molecules on hydrolysis. These are further classified as **disaccharides, trisaccharides, tetrasaccharides**, etc. depending upon the number of monosaccharide units present in their molecules. For example,

• **Disaccharides** : Carbohydrates which on hydrolysis give two molecules of the same or different monosaccharides. For example, sucrose, lactose, maltose. All these have the molecular formula $C_{12}H_{22}O_{11}$.

• **Trisaccharide** : Carbohydrates which on hydrolysis give three molecules of the same or different monosaccharides. For example, raffinose $C_{18}H_{32}O_{16}$.

• **Tetrasaccharides** : Carbohydrates which on hydrolysis give four molecules of the same or different monosaccharides. For example, stachyose ($C_{24}H_{42}O_{21}$).

(ii). **Polysaccharides**. These are carbohydrates which are polymeric and can be hydrolysed to give a large number of monosaccharide units. The common examples are **cellulose, starch, glycogen**, etc. The general formula of starch and cellulose is $C_6H_{10}O_5$. These get hydrolysed to give monosaccharides.

- In general, monosaccharides and oligosaccharides are crystalline solids, soluble in water and sweet in taste. Therefore, these are collectively called **sugars**.
- Polysaccharides are amorphous, insoluble in water and tasteless and are, therefore, known as **non-sugars**.

MONOSACCHARIDES

Monosaccharides are polyhydric aldehydes and ketones which cannot be hydrolysed into simpler carbohydrates. The monosaccharides are classified as:

(i) **Aldoses.** The monosaccharides containing an aldehyde (CHO) group are called aldoses. This group (CHO) is always present at one end of the carbon chain, i.e., at C_1 .

(ii) **Ketoses.** The monosaccharides containing a keto ($\text{C}=\text{O}$) group are called ketoses. In all naturally occurring ketoses keto group is present at a carbon next to the terminal carbon, i.e., at C_2 .

They are further classified as *trioses*, *tetroses*, *pentoses*, *hexoses*, *heptoses*, etc. depending upon the number of carbon atoms they contain. Therefore, while naming these mono saccharides, the prefix indicating the number of carbon atoms like *tetra* (4), *penta* (5), *hexa* (6), *hepta* (7) etc. is incorporated in the term aldose or ketose. For example, an *aldopentose* means that it is an aldehydic carbohydrate containing five carbon atoms. Similarly *ketohexose* means a ketone containing six carbon atoms.

The common monosaccharides are given in Table 1.

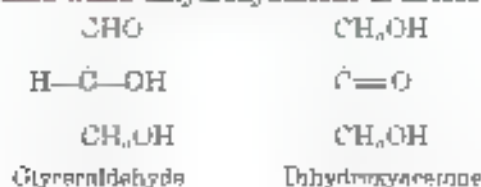
Table 1 Monosaccharides

No. of Carbon atoms	Class	Molecular formula	Structural formula	Examples
Aldoses				
3	Aldotrioses	$\text{C}_3\text{H}_6\text{O}_3$	$\text{CH}_2\text{OHCHOHCHO}$ /	Glyceraldehyde
4	Aldotetroses	$\text{C}_4\text{H}_8\text{O}_4$	$\text{CH}_2\text{OH}(\text{CHOH})_2\text{CHO}$	Erythrose, Threose
5	Aldopentoses	$\text{C}_5\text{H}_{10}\text{O}_5$	$\text{CH}_2\text{OH}(\text{CHOH})_3\text{CHO}$	Arabinose, Ribose, Xylose, Lyxose
6	Aldohexoses	$\text{C}_6\text{H}_{12}\text{O}_6$	$\text{CH}_2\text{OH}(\text{CHOH})_4\text{CHO}$	Glucose, Galactose, Mannose, Allose, Talose, Gucose, Idose, etc.
7	Aldoheptoses	$\text{C}_7\text{H}_{14}\text{O}_7$	$\text{CH}_2\text{OH}(\text{CHOH})_5\text{CHO}$	
Ketoses				
3	Ketotrioses	$\text{C}_3\text{H}_6\text{O}_3$	$\text{CH}_2(\text{CO})\text{CH}_2\text{OH}$	Dihydroxyacetone
4	Ketotetroses	$\text{C}_4\text{H}_8\text{O}_4$	$\text{CH}_2\text{OHCOCHOHCH}_2\text{OH}$	Erythrulose
5	Ketopentoses	$\text{C}_5\text{H}_{10}\text{O}_5$	$\text{CH}_2\text{OHCO}(\text{CHOH})_2\text{CH}_2\text{OH}$	Ribulose, Xylulose
6	Ketohexoses	$\text{C}_6\text{H}_{12}\text{O}_6$	$\text{CH}_2\text{OHCO}(\text{CHOH})_3\text{CH}_2\text{OH}$	Fructose, Sorbose, Tagatose, Psicose
7	Ketoheptoses	$\text{C}_7\text{H}_{14}\text{O}_7$	$\text{CH}_2\text{OHCO}(\text{CHOH})_4\text{CH}_2\text{OH}$	

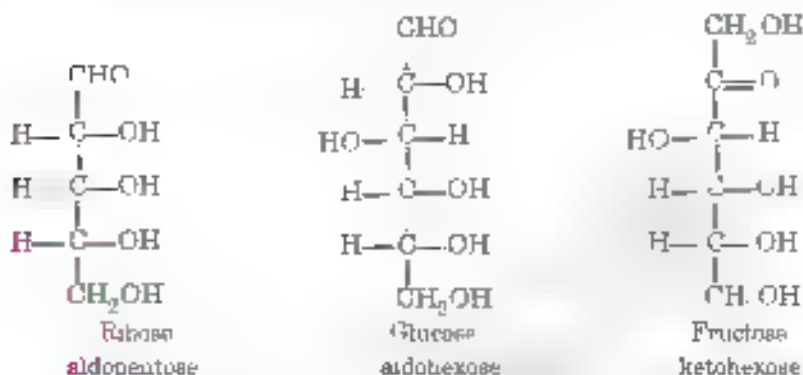
Most of the monosaccharides occur in nature. They are colourless, crystalline solids, soluble in water and have sweet taste. These are quite stable and do not get hydrolysed. They char on heating giving characteristic smell. They are optically active.

Structures of Monosaccharides

The simplest monosaccharides are trioses such as *glyceraldehyde* and *dihydroxyacetone* both having the molecular formula $\text{C}_3\text{H}_6\text{O}_3$. The glyceraldehyde is aldose while dihydroxyacetone is ketose as shown below.



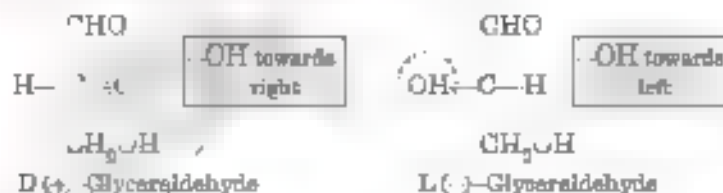
The most well-known monosaccharides are ribose $C_5H_{10}O_5$, glucose $C_6H_{12}O_6$ and fructose $C_6H_{12}O_6$. Ribose is aldopentose, glucose is aldohexose while fructose is ketohexose as shown below.



► The letter D or L carbohydrates represents configuration. By convention, a molecule is assigned D-configuration if the -OH group attached to the carbon adjacent to the -CH₂OH group (last chiral carbon) is on the right hand side irrespective of the position of other groups. On the other hand, the molecule is assigned L-configuration if the -OH group attached to the carbon adjacent to the -CH₂OH group is on the left.

D- and L-Designations

The sugars are divided into two families the *D-family* and *L-family* which have definite configurations. These configurations are represented with respect to glyceraldehyde as the standard. The glyceraldehyde may be presented by two forms as.

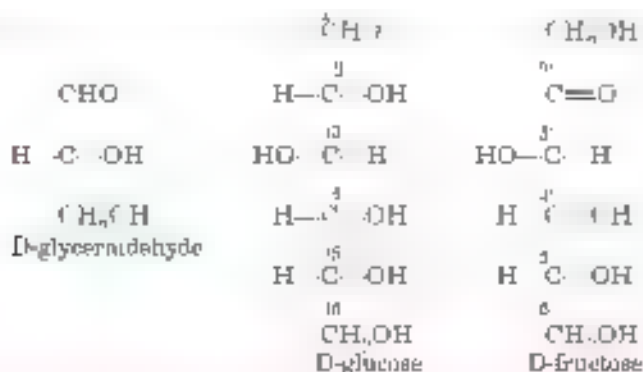


The D-configuration has -OH attached to the carbon adjacent to -CH₂OH on **right** while L-configuration has -OH attached to the carbon adjacent to -CH₂OH on **left**. The sugars are called D- or L- depending upon whether the configuration of the molecule is related to D-glyceraldehyde or L-glyceraldehyde.

It has been found that all naturally occurring sugars belong to D-series e.g., D-glucose, D-ribose and D-fructose.

However it may be **noted** that D- and L- do not represent dextrorotatory or levorotatory. The optical activity of the molecule is represented by + and - which represent the direction of rotation of plane polarized light whether dextrorotatory or levorotatory.

The carbon atoms of an aldose are **numbered** starting from the aldehyde group (-CHO), and that of ketose from that end which is closest to the ketonic group.

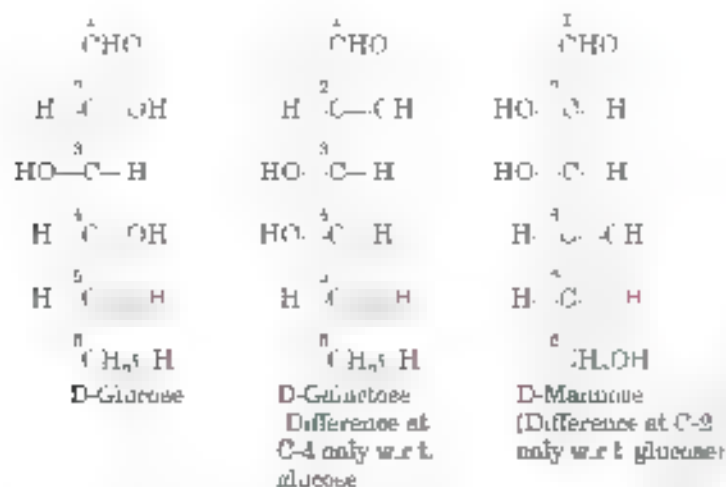


-OH group attached to last chiral C atom is projected to the **RIGHT**

Presence of Asymmetric Carbon Atoms

On carefully examining the monosaccharide molecules, we observe that they contain one or more chiral carbon atoms. For example, glucose has four chiral carbon atoms (carbons 2, 3, 4 and 5). We know that if there are n chiral carbon atoms in a molecule, it will have 2^n optical isomers. Therefore, glucose has 2^4 or sixteen optical isomers. Three of these sixteen aldohexoses which occur D-glucose, D-galactose and D-mannose.

Most naturally occurring sugars are of the D-series with the -H group of the bottom asymmetric carbon on the **right** in the Fischer projection.



It may be noted in all these three molecules, the configuration at C-5 is same (-OH on the right) and, therefore, they belong to D-family.

Glucose

Glucose occurs in nature in free as well as in the combined form. It is present in sweet fruits and honey. Ripe grapes contain about 20% of glucose and that is why it is also known as **grape sugar**. In the combined form, glucose occurs in abundance in cane sugar and polysaccharides such as starch and cellulose.

Preparation of Glucose

1. From Sucrose (Cane sugar)

When sucrose is boiled with dilute HCl or H_2SO_4 in alcoholic solution, glucose and fructose are obtained in equal amounts.



2. From Starch

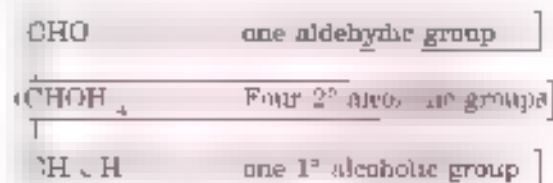
Glucose is produced commercially by the hydrolysis of starch by boiling it with dilute H_2SO_4 at 393 K under pressure of 2–3 atm.



In this process, an aqueous solution of starch obtained from corn is acidified with dil. H_2SO_4 . It is then heated under 2–3 atm pressure steam in autoclave. When the hydrolysis is complete, the liquid is neutralised with sodium carbonate to a pH of 4–5. The resulting solution is concentrated under reduced pressure to get the crystals of glucose.

Structure of glucose

Glucose is an aldohexose. It is also known as dextrose. It is monomer of many of the larger carbohydrates such as starch, glycogen, cellulose etc. It is probably the most abundant compound on the earth. It has one aldehyde group, -CHO , one primary alcohol group $\text{-CH}_2\text{OH}$ and four secondary alcohol groups -CHOH- . Its structure may be written as



This structure was assigned on the basis of the following evidences

1. Molecular formula

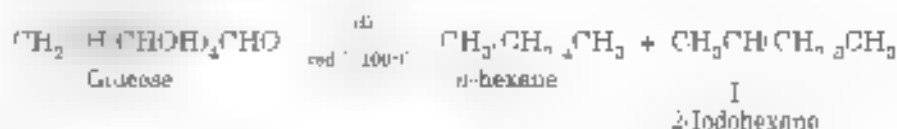
The molecular formula of glucose has been found to be $\text{C}_6\text{H}_{12}\text{O}_6$

2. Straight chain structure

i. When aqueous solution of glucose is treated with sodium amalgam Na/Hg or sodium borohydride NaBH_4 it is reduced to sorbitol or glucitol, a hexanary alcohol.



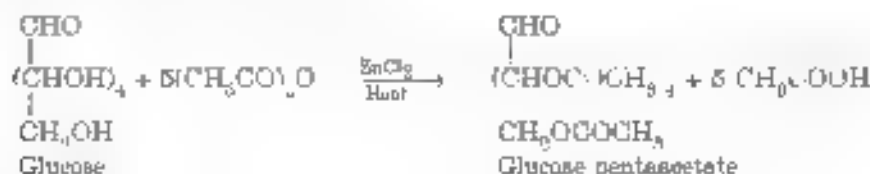
ii. Prolonged heating with hydroiodic acid and red phosphorus at 100°C gives a mixture of *n*-hexane and 2-iodohexane.



The formation of *n*-hexane suggests that all the six carbon atoms in glucose are arranged in a straight chain structure of glucose.

3. Presence of five hydroxyl -OH groups

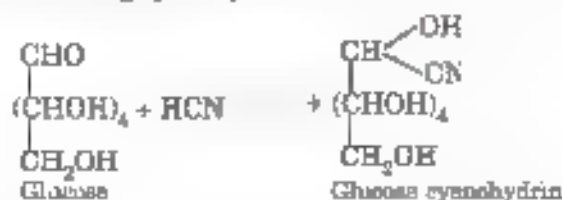
i. **Acetylation.** Glucose reacts with acetic anhydride in the presence of anhydrous zinc chloride to form glucose pentaacetate or penta acetyl glucose. This is known as acetylation of glucose.



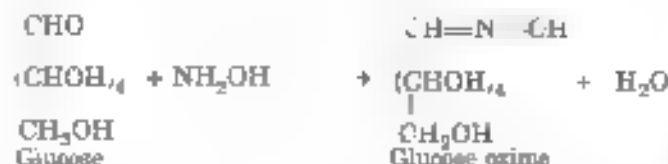
The formation of penta-acetyl derivative confirms the presence of five -OH groups in glucose molecule. We know that the presence of two or more -OH groups on the same carbon atom makes the molecule unstable. Now, since glucose exists as a stable compound, this shows that five -OH groups should be attached to different carbon atoms.

4. Presence of an aldehyde (-CHO) group

(i) **Reaction with hydrogen cyanide.** Like aldehydes, glucose reacts with hydrogen cyanide forming cyanohydrin.



(iii) **Action with hydroxylamine.** Glucose reacts with hydroxylamine NH_2OH to form glucose oxime.



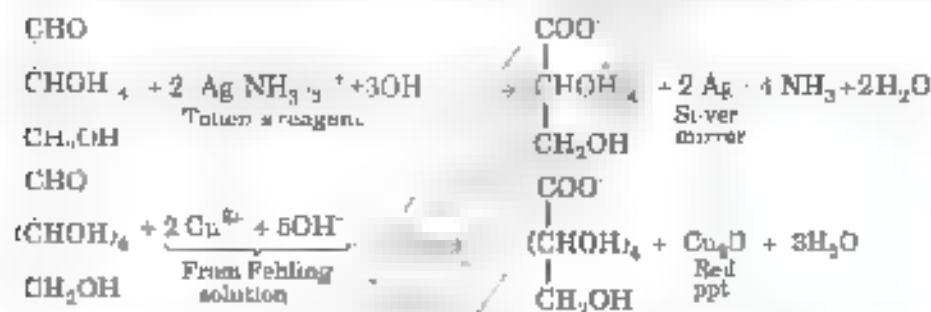
These reactions suggest that glucose contains a carbonyl (C=O) group.

6. Oxidation of glucose. The oxidation of glucose occurs as:

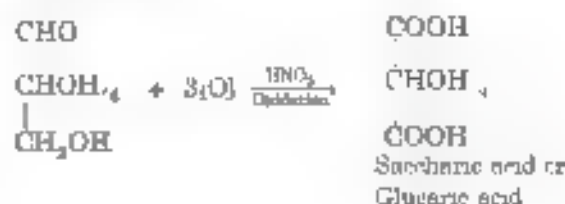
Glucose gets oxidised to six carbon carboxylic acid, gluconic acid on reaction with a mild oxidising agent like bromine water. This indicates that the carbonyl group is present as an aldehyde (-CHO) group.



Since glucose is readily oxidised, it acts as a strong reducing agent and reduces Tollens reagent, ammoniacal silver nitrate and Fehling solution.



Strong oxidising agents like nitric acid oxidise both the terminal groups -CHO and -CH₂OH of glucose to give the dibasic acid, saccharic acid (also known as gluconic acid). This indicates the presence of a primary alcohol (-OH) group in glucose.

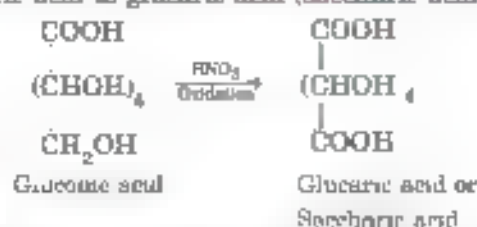


! U Curious...



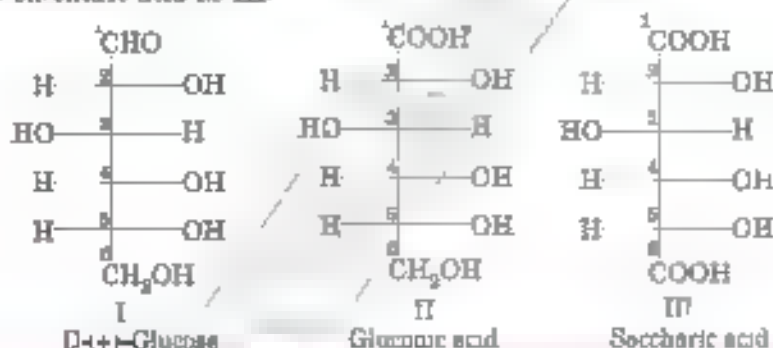
- Why is glucose given to patients under exhaustion?
- ▶ Glucose is an instant source of energy and therefore is given to patients under exhaustion.

Gluconic acid obtained by the oxidation of glucose with $\text{Br}_2/\text{H}_2\text{O}$ also gets oxidised with nitric acid to glucaric acid (saccharic acid).



It may be noted that in glucose, the OH group at C_2 chiral carbon is oriented towards left while the remaining three OH groups at C_3 , C_4 and C_5 chiral carbon atoms are oriented towards right.

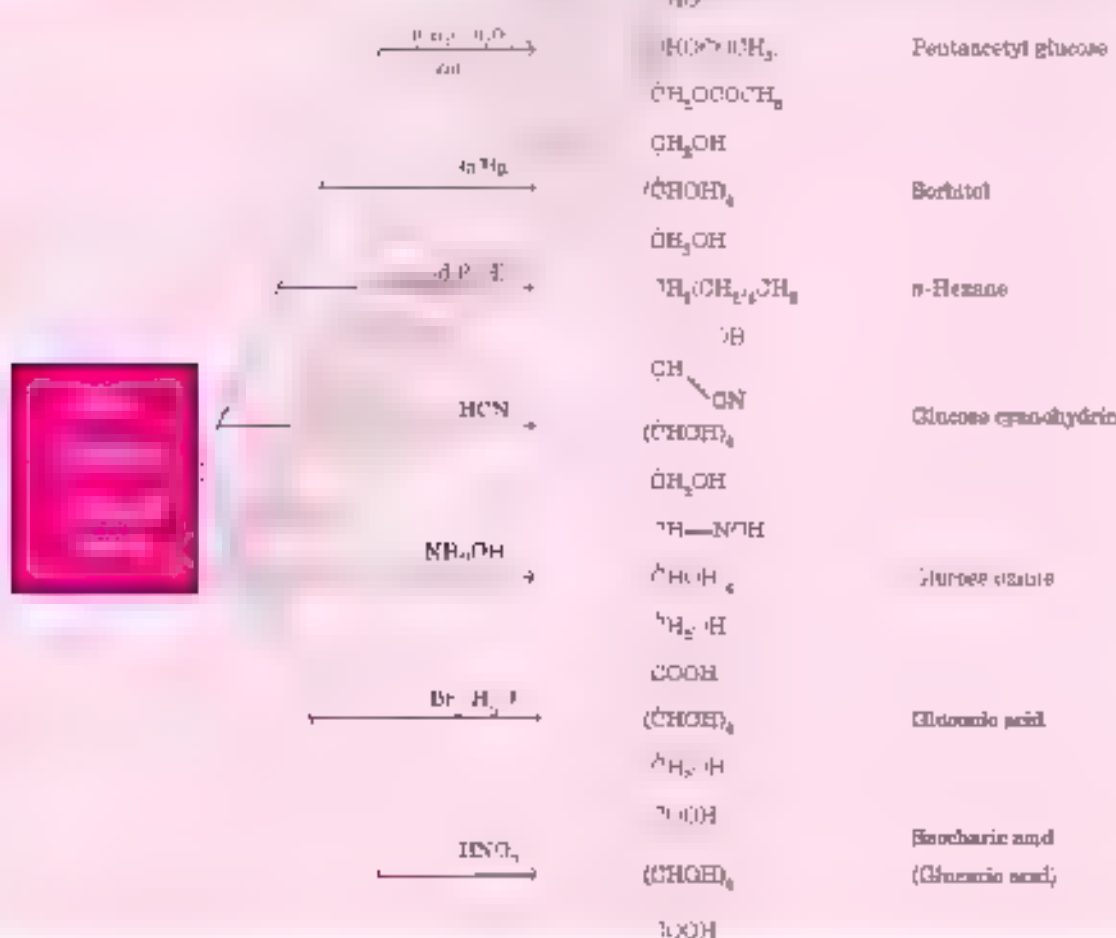
On the basis of above reactions, Fischer assigned an open chain structure of glucose shown below as structure I. Similarly, glucuronic acid is represented as II and saccharic acid as III.



Glucose is correctly named as D-+ glucose. D before the name of glucose represents the configuration as already discussed whereas + represents dextrorotatory nature of the molecule.

SUM UP

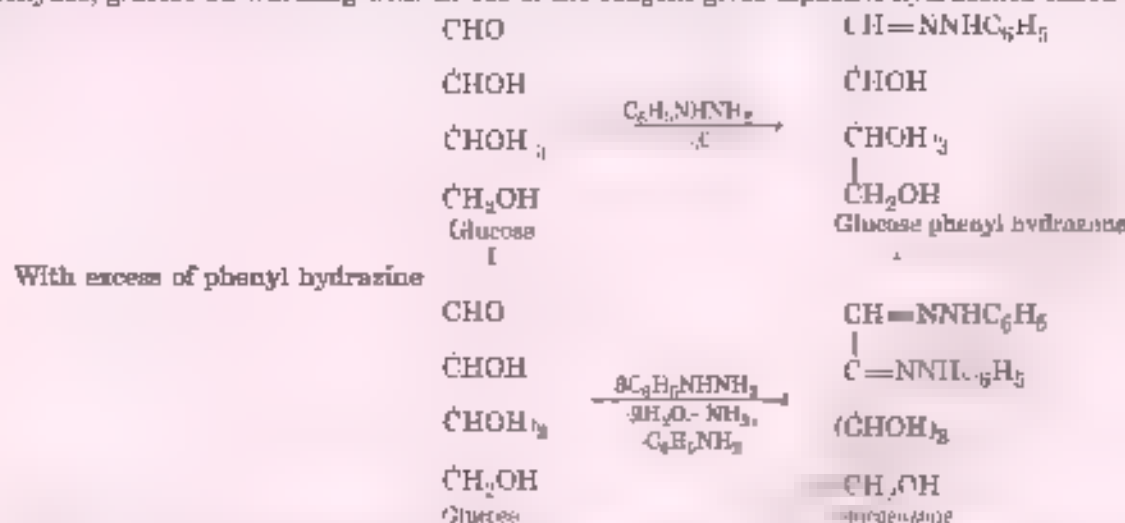
The important reactions of glucose are summed up as



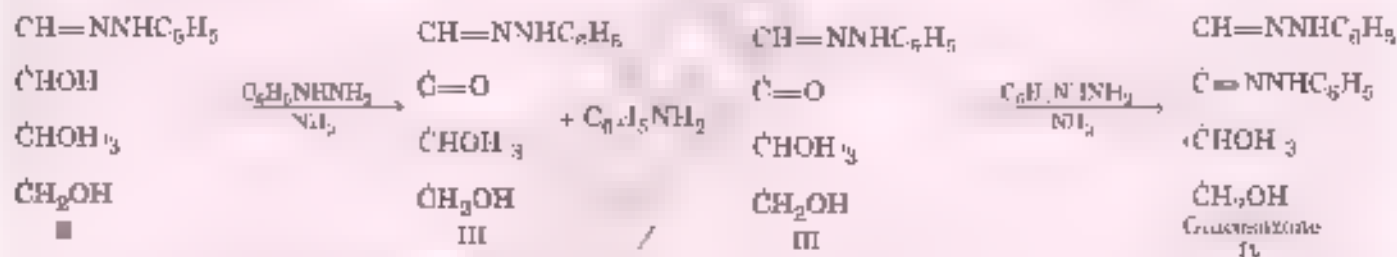
Learning Plus

Reactions with phenyl hydrazine : Osazone formation.

Glucose reacts with phenyl hydrazine like normal aldehydes to form phenyl hydrazone. However unlike normal aldehydes, glucose on warming with excess of the reagent gives diphenyl hydrazones called **osazones**.

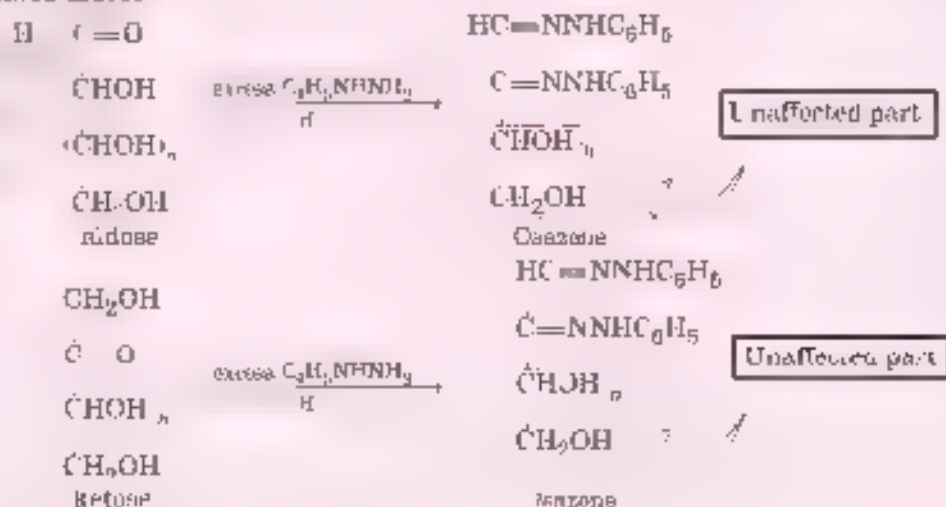


It has been observed that during the reaction, three equivalents of the reagent are consumed, but the product contained only two phenyl hydrazone residues. It has been found that after the formation of phenyl hydrazone II, the adjacent -CHOH group is oxidised by a second phenyl hydrazine molecule to carbonyl group III and itself is reduced to aniline and ammonia. Phenyl hydrazone of glucose II thus produced reacts with phenyl hydrazine to form glucosazone.



Glucosazone is a yellow crystalline solid compound, sparingly soluble in water and has a sharp melting point. It is used in the identification of glucose.

In the reaction of glucosazone both I and C are converted to phenyl hydrazine. Therefore a ketose also gives the same osazone as its related aldose.



Thus, if an aldose and ketose forms the same osazone, they have the same structure at all carbons except C₁ and C₂. For example, glucose and fructose form the same osazone.

Cyclic Structure of D-Glucose

The open chain structure of glucose explained most of its properties. However, it could not explain the following facts.

1 Despite having an aldehydic CHO group, **glucose does not undergo certain characteristic reactions of aldehydes**. For example,

a) Glucose does not react with sodium bisulphite NaHSO_3 to form addition product.

b) Glucose does not react with ammonia.

c) Glucose does not give Schiff's test and 2,4-DNP test like other aldehydes.

2 **Glucose reacts with hydroxylamine ($-\text{NH}_2\text{OH}$) to form an oxime but glucose pentaacetate does not react with hydroxylamine**. This shows that $-\text{CHO}$ group is not present in glucose pentaacetate.

3. **D (+)-Glucose exists in two stereoisomeric forms i.e., α -D-glucose and β -D-glucose**. These two forms are crystalline and have different melting points and optical rotations. When glucose was crystallized from a concentrated solution at 303 K it gave α -form of glucose having melting point 419 K or 146°C and $[\alpha]_D = +11.1^\circ$. On the other hand, the β -form of glucose is obtained on crystallisation of glucose from a hot saturated solution at a temperature above 371 K. The β -form of glucose has melting point 423 K (or 150°C) and $[\alpha]_D = +19.2^\circ$.

4 **Mutarotation**. When either of the two forms of glucose (α -D-glucose and β -D-glucose) are dissolved in water and allowed to stand, these get slowly converted into other form and a equilibrium mixture of both α -D-glucose (about 36%) and β -D-glucose (about 64%) is formed.



The formation of equilibrium mixture can be explained as

The α -D-glucose has a specific rotation of $+11.1^\circ$ while β -D-glucose has a specific rotation of $+19.2^\circ$. When α form is dissolved in water, its specific rotation falls until a constant value of $+52.6^\circ$ is reached. On the other hand, when β -form is dissolved in water its specific rotation increases and becomes constant at $+52.6^\circ$.

This spontaneous change in specific rotation of an optically active compound with time to an equilibrium value is called mutarotation. (Latin, *mutare* means to change).

Thus, there is an equilibrium mixture of α - and β -forms in the solution.



5. **Glucose forms isomeric methyl glucosides**. When glucose is heated with methanol in the presence of dry hydrogen chloride gas, it gives two isomeric monomethyl derivatives known as methyl α -D-glucoside (m.p. = 438 K or 165°C) and methyl β -D-glucoside (m.p. = 380 K or 107°C).



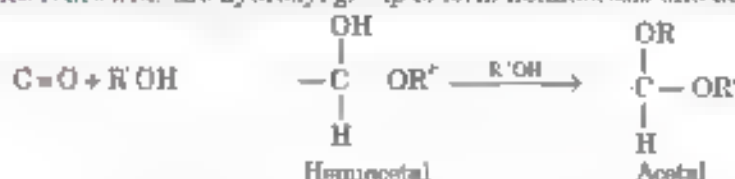
These two glucosides do not reduce Fehling's solution and also do not react with hydrogen cyanide or hydroxy amine indicating that the free $-\text{CHO}$ group is not present.

Since only one molecule of methanol is used for the formation of methyl glucoside, these must be hemiacetals. These results show that glucose does not have open chain form structure. Like glucose the open chain structures of other monosaccharides, aldoses and ketoses show similar limitations.

Cyclic Structures of Monosaccharides

The monosaccharides give the characteristic reactions of alcohols and carbonyl group (aldehydes and ketones). It has been found that these monosaccharides exist in the form of cyclic structures. We know that aldehydes

and ketones react with the hydroxyl group to form hemiacetals and acetals, as



Monosaccharides contain a number of $-\text{OH}$ groups and an aldehyde or a keto group. Therefore, they can undergo *intramolecular reaction* within the molecule to form hemiacetals which result in *cyclic structures*. In cyclization, the $-\text{OH}$ groups generally of C_5 or C_6 in aldoses and C_5 or C_6 in ketoses combine with the aldehyde or keto groups. As a result cyclic structures of five or six membered rings containing one oxygen atom are formed. For example, glucose forms a ring structure. It forms a six membered ring of five carbon atoms and one oxygen atom.

Cyclic Structure of Glucose

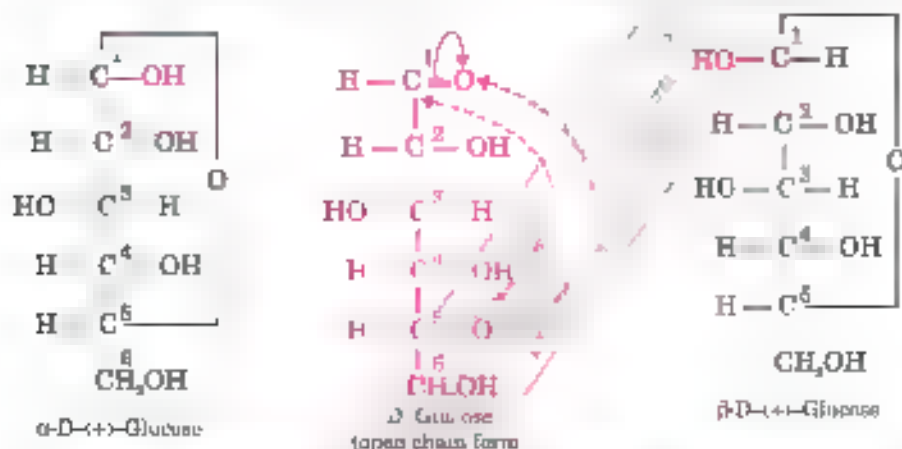
Anomers

Glucose forms a hemiacetal between the $-\text{CHO}$ group and the $-\text{OH}$ group on the C_5 atom. As a result, of cyclization C_1 becomes asymmetric chiral and the newly formed $-\text{OH}$ group may be either on the left or on the right in Fischer projection formulae. This results in the formation of two isomers which differ in the orientation of H and $-\text{OH}$ groups around C_1 atom. These isomers are known as α -D-glucose and β -D-glucose.

The isomer having the hydroxyl group $-\text{OH}$ on the right is called α -D-glucose and the isomer having the hydroxyl group $-\text{OH}$ on the left is called β -D-glucose.

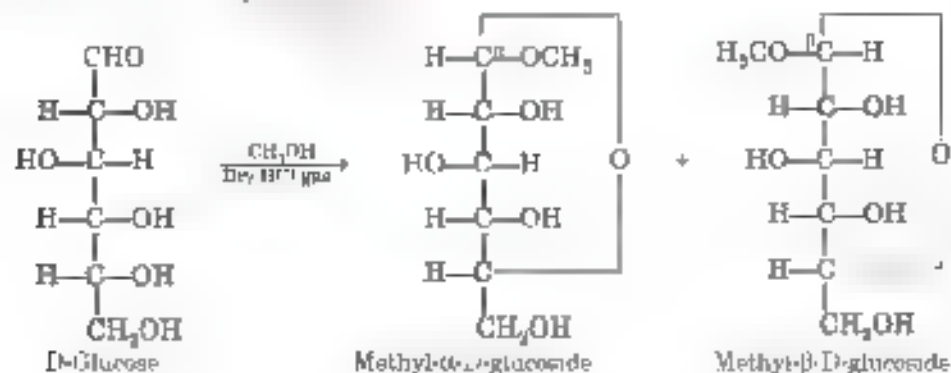
Such pairs of optical isomers which differ in the configuration only around C_1 atom are called **anomers**.

These two forms are not mirror images of each other and, hence, are not enantiomers. The C_1 carbon is known as **anomeric carbon** or **glycosidic carbon**.



The above representations are called **Fischer projection formulae**.

The formation of two methyl glucosides by reaction of glucose with methanol can be explained as

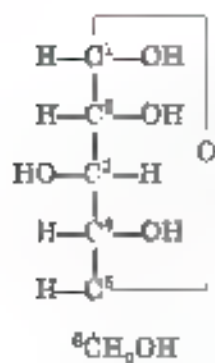


REMEMBER

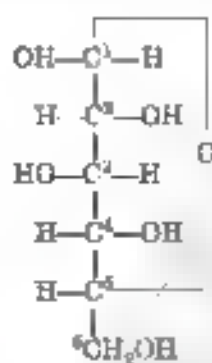
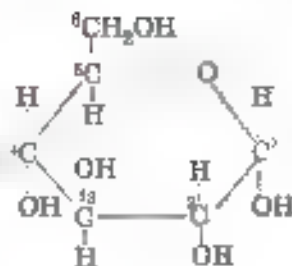
- In α -D-glucose, the OH group on C_1 is on right and
- in β -D-glucose, the OH group on C_1 is on left

Such pairs of optical isomers which differ in the configuration only around C_1 atom are called **anomers**.

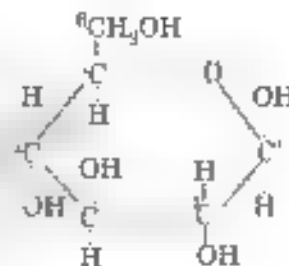
Structure of g_{max}



(d) D₁ + z = 0 *implies* *(e) D₁ + z = 0*



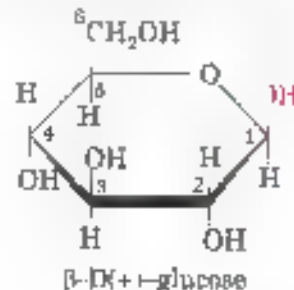
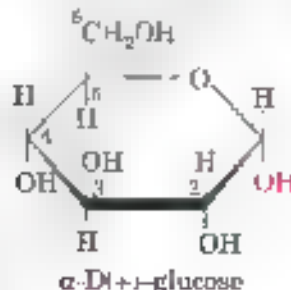
β -D-(+)-Glucose
or β -D-(+)-glucopyranose



- Groups on the right in a Fischer projection are down in a Haworth projection and
- Groups on the left in a Fischer projection are up in a Haworth projection

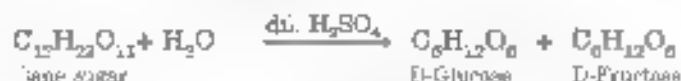
To write pyranose structures for any monosaccharide α - and β -D-glucose, draw a hexagon with its oxygen atom at the upper right hand corner. The terminal ^4H - ^1H group is always placed above the plane of the hexagon ring in D-isomers. Place all the groups on C^1 , C^2 , and C^3 which are present in the left hand side in Fischer projection above the plane of the ring and all these groups on the right hand side below the plane of the ring.

These two structures for summarizing may also be represented as



Fructose occurs in fruits and is called **fruit sugar**. It is also present in honey and sweet fruits along with glucose. In the combined state, it is also present in disaccharide (sucrose) and polysaccharide (maltose).

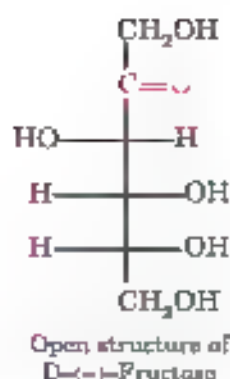
It is obtained alongwith glucose by hydrolysis of cane sugar with dilute H_2SO_4 .



The solution having equal molecules of L-glucose and D-fructose is called **invert sugar**.

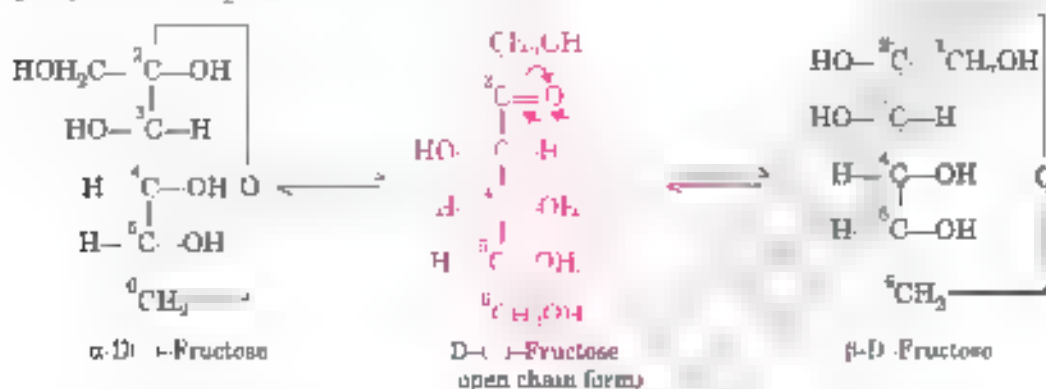
Structure of Fructose

Its molecular formula is $C_6H_{12}O_6$. On the basis of its reactions it has been established that fructose contains a keto group at C-2 and the six carbon atoms are arranged in a straight chain as in case of glucose. It belongs to D-series and is a meso-rotatory compound. It is also called **levulose**. Therefore it is written as D-(-)-fructose. It is a pentahydroxy ketone and its open chain structure is shown ahead:

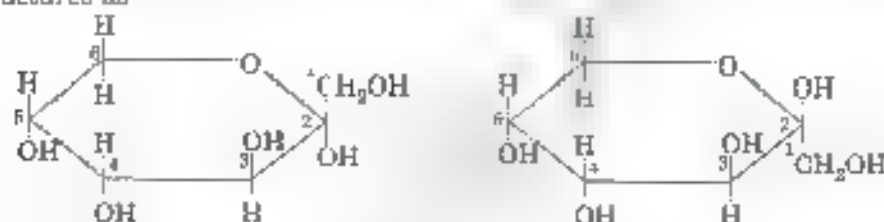


Cyclic Structure

Like glucose, fructose also has a cyclic structure. The hemiacetal is formed by the intramolecular combination of C_2 keto group and -OH group of C_5 atom. As a result, C_5 atom becomes asymmetric and therefore, D-fructose has two possible isomers α -D-(+)-fructose and β -D-(+)-fructose which differ in the arrangement of CH_2OH , H and -OH groups around C_5 . These are shown below:

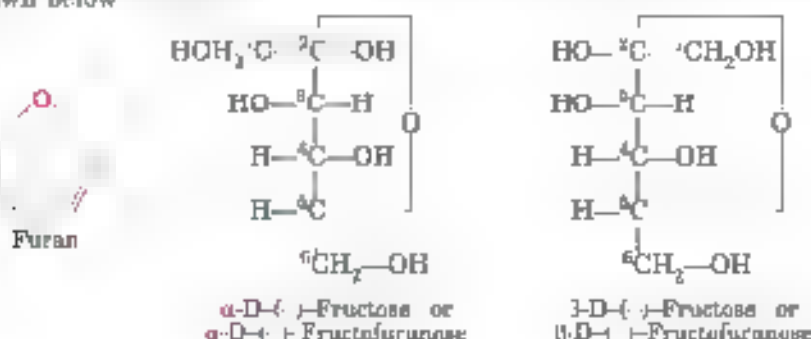


The above structures may be written in the **Haworth formula** as pyranose ring structures as

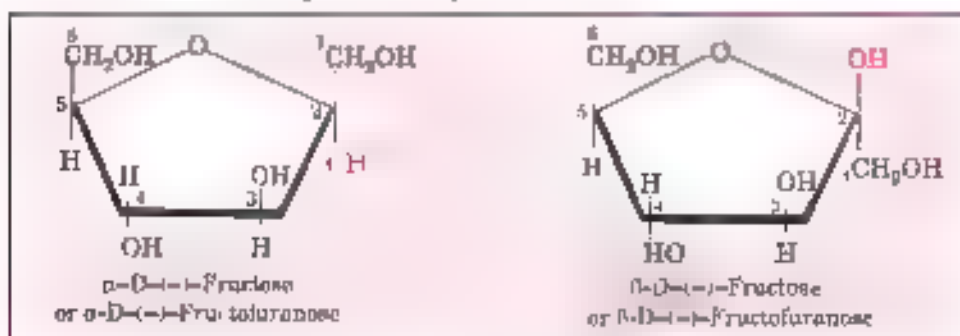


α -D-(+)-Fructose or α -D-(+)-Fructopyranose / β -D-(+)-Fructose or β -D-(+)-Fructopyranose

In the free state, D-fructose exists as a six membered ring or as pyranose ring. However, in the combined state as a component of disaccharides, it exists in the **furanose form** (5-membered hemiacetal). This structure is similar to furan ring which is a five membered heterocyclic ring with one oxygen atom. The furanose structure can be obtained by internal ketal formation by combining keto group of C_2 and -OH group of C_5 as shown below:



These structures may also be represented as



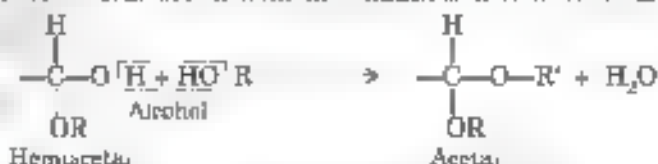
These cyclic structures for other monosaccharides can also be written in the same way as for glucose.

DISACCHARIDES

Disaccharides are the carbohydrates which on hydrolysis give two same or different monosaccharides. Their general formula is $C_{12}H_{22}O_{11}$. The important members belonging to disaccharides are *sucrose*, *maltose* and *lactose*. On hydrolysis with dilute acids or enzymes these give the following two molecules of monosaccharides.



The disaccharides are made up of two molecules of monosaccharides linked to each other by the condensation reaction. The linking is formed just as hemiacetals react with alcohols to form acetals with the elimination of a water molecule.

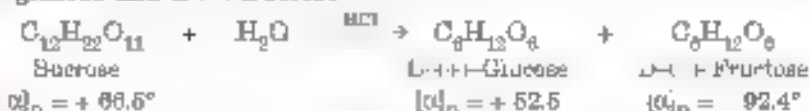


The linkage between two monosaccharide units through oxygen atom is called **glycosidic linkage**.

In a similar way, the hydroxyl groups of hemiacetals of two monosaccharide units condense to form disaccharide. The two monosaccharide units are linked to each other through oxygen atom by a bond called **glycosidic linkage**. Let us discuss these briefly.

1. Sucrose

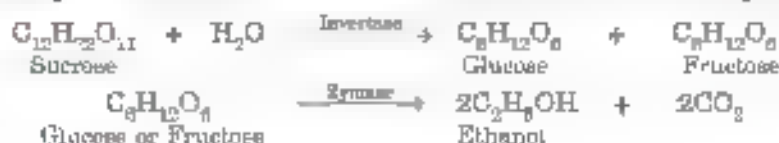
It is the most common disaccharide and is widely distributed in plants particularly sugar cane and sugar beet. It is manufactured either from cane sugar or sugar beet. The sugar obtained from sugar beet is called **beet sugar**. It is a colourless crystalline and sweet substance. It is very soluble in water and its aqueous solution is dextrorotatory having $[\alpha]_D^{20} = +66.5^\circ$. On hydrolysis with dilute acids or enzyme invertase cane sugar gives equimolar mixture of D-(+)-glucose and D-(+)-fructose.



So, sucrose is dextrorotatory but after hydrolysis gives dextrorotatory glucose and laevorotatory fructose. D-(+)-fructose has a greater specific rotation than D-(+)-glucose. Therefore the resultant solution upon hydrolysis is laevorotatory in nature with specific rotation of -36.9° . Since there is change in the sign of rotation from dextro before hydrolysis to laevo after hydrolysis, the reaction is called **inversion reaction** and the mixture glucose and fructose is called **invert sugar**.

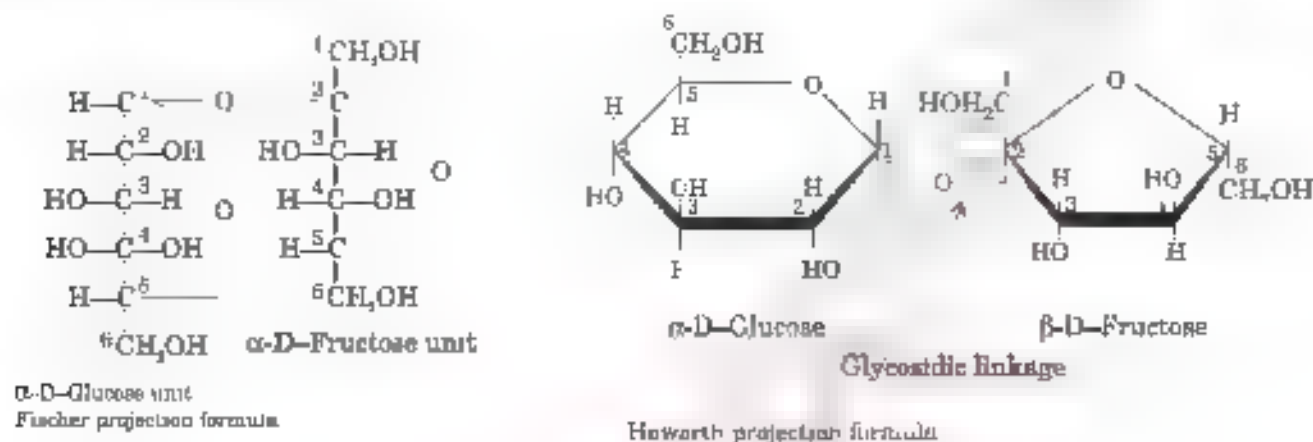
Bacteria present in the mouth have an enzyme which converts starch into a polysaccharide called dextran. About 10% of dental plaque is composed of dextran. That is why dentists caution you not to eat candy.

Sucrose is formed by yeast when the enzyme **invertase** hydrolyses the sucrose to glucose and fructose and enzyme **zymase** converts these monosaccharides to ethanol (ethyl alcohol).



Structure

Sucrose is composed of D-glucose and β -D-fructose. These units are held together by α , β -glycosidic linkage between C_1 of the glucose unit (pyranose ring) and C_2 of the fructose unit (furanose ring). This structure was proposed by Haworth (1927).



C_1 of α -glucose unit is linked to C_2 of β -fructose unit.

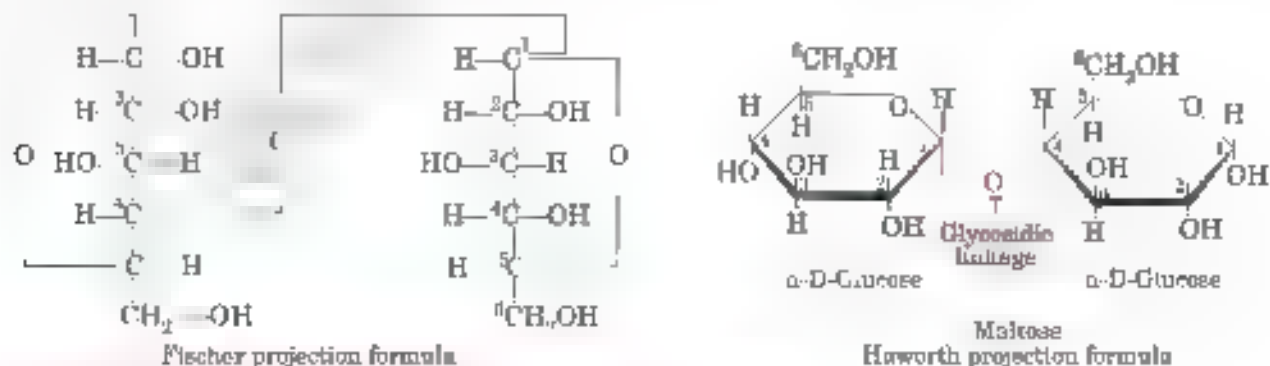
2. Maltose

It is known as malt sugar. It is the principal disaccharide obtained by the partial hydrolysis of starch by diastase, an enzyme present in malt (sprouted barley seeds).



Structure

On hydrolysis, one mole of maltose gives two moles of α -D-glucose. It is a reducing sugar. It is composed of two α -D-glucose units which are condensed together through C_1 of one unit and C_4 of the other unit. Both glucose units are in **pyranose form**.



C_1 of one glucose unit is linked to C_4 of other glucose unit.

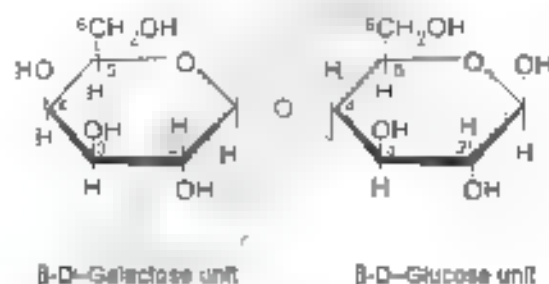
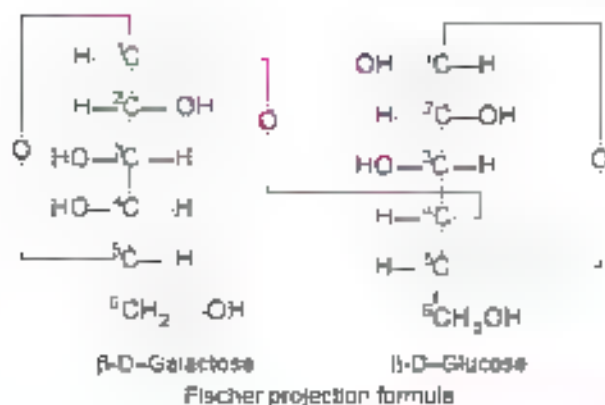
3. Lactose

Lactose occurs in milk and, therefore, it is also called **milk sugar**.

Structure

Lactose on hydrolysis with dilute acid gives equimolar mixture of β -D-glucose and β -D-galactose. It is a reducing sugar. Therefore, it is composed of β -D-glucose and β -D-galactose units. These units are held together by glycosidic linkage between C_1 of galactose and C_4 of the glucose unit.

Lactose gets hydrolysed by enzyme (an enzyme which specifically hydrolyses β -glycosidic linkages).

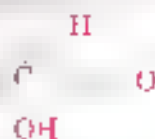


C_1 of galactose is linked to C_4 of glucose unit.

Reducing and non-reducing sugars

Reducing sugars. The saccharides which reduce Fehling's solution and Tollen's reagent are called **reducing sugars**. The reducing sugars contain groups which can be easily oxidised by Fehling solution or Tollen's reagent. For example, they contain the following characteristic groups

Reducing sugars contain α -hydroxyaldehyde or α -hydroxy ketone groups

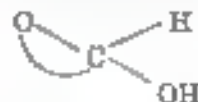


α -Hydroxy aldehyde group



α -Hydroxy ketone group

If reducing sugars contain cyclic hemiacetal or hemiketal groups. In aqueous solutions these hemiacetals or hemiketals exist in equilibrium with relatively small concentration of non-cyclic aldehydes or α -hydroxy ketones having a free $-CHO$ or $-CO$ group.



Hemiacetal



Hemiketal

Non-reducing sugars. The saccharides which do not reduce Fehling's solution or Tollen's reagent are called **non-reducing sugars**.

These do not contain free aldehydic or ketonic group with $-OH$ group on the carbon adjacent to carbonyl group. They contain stable acetal or ketal structures. Their cyclic structures cannot be opened into an open chain form having a free carbonyl group.

Examples. All monosaccharides contain free $-CHO$ or $-C=O$ group and are reducing sugars. For example, D-glucose or D-fructose.

Among the disaccharides maltose and lactose are reducing sugars because in one of the monosaccharide units there is a hemiacetal group that can be opened to give free $-CHO$ group. Sucrose is non-reducing because the reducing groups of glucose and fructose are involved in glycosidic bond formation.

Sugar and Sweetness

The monosaccharides and disaccharides have sweet taste and, therefore, they are called sugars. The degree of sweetness, however, varies as shown below

Sugar	Relative sweetness
Lactose	18
Maltose	32
Galactose	32
Glucose	74
Sucrose	100
Fructose	178

As is clear from the table, fructose is the sweetest of all the natural sugars.

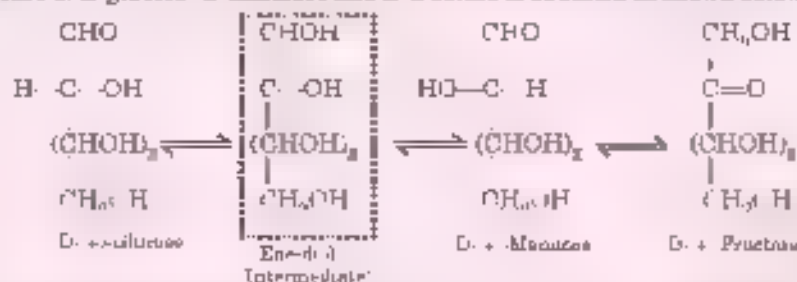
However, it may be noted that in addition to carbohydrates, some other chemical compounds are also very sweet. For example

- Saccharin used as artificial sweetener is about 500 times as sweet as sucrose.
- The protein *monkshorn* is about 3000 times sweeter than sucrose.
- The peptide *aspartame* is about 180 times sweeter than sucrose.

Learning Place

Action of alkalis on monosaccharides: Lobry de Bruyn van Ekenstein Rearrangement.

When glucose is treated with a concentrated solution of an alkali, it first turns yellow then brown and finally a brown resinous mass is formed. However, when treated with a dilute solution of an alkali, it undergoes a series of reversible keto-enol tautomerization reactions to form an equilibrium mixture of D-glucose, D-mannose and L-fructose. The rearrangement takes place through a 2-enol intermediate. This reaction is called **Lobry de Bruyn van Ekenstein rearrangement**. For example, when a solution of D-glucose containing calcium hydroxide is allowed to stand for several days, an equilibrium mixture of D-glucose, D-mannose and D-fructose is obtained as shown below:



It may be noted that the same equilibrium mixture is obtained even if one starts with D-+mannose or D-+fructose.

POLYSACCHARIDES

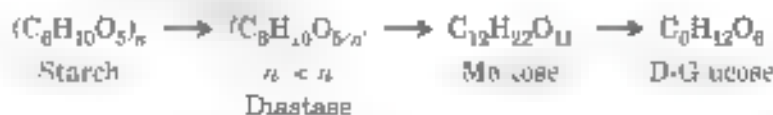
These are neutral polymeric compounds in which hundreds or even thousands of monosaccharide units are joined by **glycosidic linkages**. They have the general formula $(\text{C}_6\text{H}_{10}\text{O}_5)_n$, where n has very large value. They are colourless, tasteless and are insoluble in water. They play very important role in plant and animal life as food storage and structural role. They are usually made up of pentoses or hexoses. The important polysaccharides are **cellulose, starch, glycogen and dextrins**.

However, starch and cellulose are most important of the polysaccharides.

1. Starch (*amylum*), $(\text{C}_6\text{H}_{10}\text{O}_5)_n$

It is the main storage polysaccharide of plants. It is an important dietary source for human beings. It occurs in plants, particularly in their seeds, roots, tubers etc. The main sources are wheat, rice, maize, potatoes, barley and sorghum. It occurs in the form of **granules**, which vary in size and shape depending upon their plant source. Starch is a white powder, insoluble in cold water.

Its solution gives blue colour with iodine solution. The blue colour disappears on heating and reappears on cooling. Starch is hydrolysed with dilute acids or enzymes and breaks down to molecules of varying complexity ($n > n' > n''$) and finally gives D-glucose.



Starch is a non-reducing saccharide. It does not reduce Fehling's solution or Tollen's reagent. It also does not form an osone, indicating that all hemiacetal hydroxyl groups of glucose units are not free but are linked with glycosidic linkages.

Starch is a polymer of α -D-glucose and consists of two components: water soluble component **amylose** (15–20%) and water insoluble component **amylopectin** (80–85%).

RU Check...



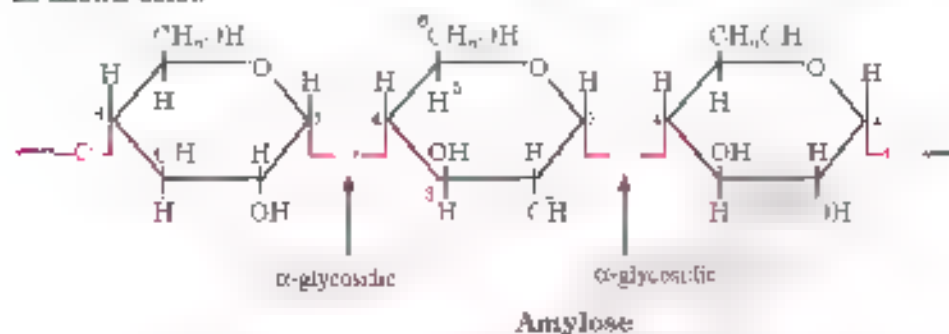
- Fructose contains a ketonic group, yet it reduces Fehling's solution and Tollen's reagent.
- Fructose although contains a keto group, yet it acts as a reducing sugar and reduces Fehling's solution and Tollen's reagent. This is because in alkaline solution fructose undergoes a complex series of reactions that lead to isomerizations known as Lobry de Bruyn van Ekenstein rearrangement forming glucose and mannose. As a result, it is in equilibrium with a mixture of glucose and mannose. Since both glucose and mannose contain -CHO group, therefore it probably reduces Tollen's reagent and Fehling solution.

REMEMBER

- A monosaccharide are reducing sugars e.g. glucose, fructose.
- Maltose and lactose are reducing sugars.
- Sucrose is a non-reducing sugar.

Sucrose is a non-reducing and is not readily oxidised as a reducing sugar. Therefore, it is much more useful for preserving foods such as jams and jellies. A reducing sugar like glucose would oxidise and spoil the food.

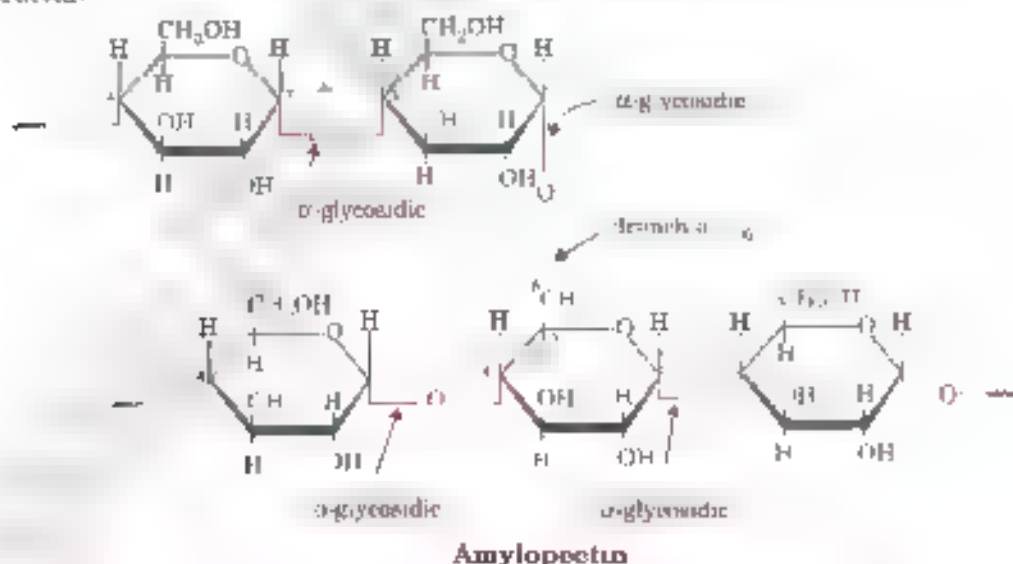
α Amylase. It is a water soluble fraction. It is a linear polymer of α -D-glucose. It contains about 200-1000 α -D-glucose units which are linked to one another through α -glycosidic linkage involving C_1 of one glucose and C_4 of the next as shown below



C_1 of one glucose unit is linked to C_4 of next glucose unit.

Its molecular mass can range from 10,000 to 500,000.

Amylopectin. It is a water soluble fraction. It is a highly branched chain polymer which does not give blue colour with iodine. It consists of a large number several hundreds of short chains of 25-30 D glucose units. In this case, the main chain involves linkages between C_1 of one α -D-glucose unit and C_4 of the other. The C_1 of terminal glucose at each chain is further linked to C_6 of the other glucose unit in the next chain through C_1-C_6 α -linkage. This gives highly branched structure.



C_1 of one glucose unit is linked to C_4 of other glucose unit.
 C_1 of terminal glucose unit is linked to C_6 of other glucose unit.
 Thus chain is formed by C_1-C_4 glycosidic linkage and branching occurs by C_1-C_6 glycosidic linkage.

For simplicity it may also be represented as shown below



Representation of branched chain structure of amylopectin
 each • represents a glucose unit

Starch is used as the principal food storage of glucose energy. It is hydrolysed by enzyme amylase present in saliva. The end product is glucose which is an essential nutrient.

2. Cellulose ($C_6H_{10}O_5)_n$

It is also major structural polysaccharide in higher plants where it constitutes the bulk of cell wall. It is probably the most abundant organic substance found in plant kingdom. Over 50% of the total organic matter in the living world is cellulose. Dry leaves contain 10–20% cellulose, wood contains 30% and cotton contains 90% cellulose. Cellulose forms the fibrous component of plant cell walls. Cellulose does not reduce Fehling solution or Tollen's reagent. It does not form osazone and is not fermented by yeast. It is not hydrolysed so readily as starch, but on heating with dilute sulphuric acid under pressure gives D-glucose.

Structurally cellulose is a straight chain polysaccharide composed of many β -D-glucose units, which are joined by **β -glycosidic linkages** between C1 of one glucose unit and C4 of the next glucose unit. The chains are arranged to form bundles and are held together by hydrogen bonds between glucose units of adjacent strands. Its molecular mass is in the range of 50,000–500,000 (about 300–2500 D-glucose units).

Cellulose is an industrially important compound. It finds uses in textiles, paper and plastic industries. When treated with a wide variety of chemicals, it forms many useful products (celluloid, rayon, gun cotton, an explosive, cellulose acetate, plastics and wrapping films), methyl cellulose (fabric sizing, pastes and emulsions), ethyl cellulose (plastic resins and films), etc.

Digestion of Cellulose

Cellulolytic bacteria, present in the stomachs of ruminants (grazing animals e.g. cow, buffalo, deer, sheep, etc.) break down cellulose with the help of enzyme **cellulase**. It is then digested and converted into glucose. Therefore, grazing animals can use cellulose of grass and plants as food by converting them into glucose.

3. Glycogen ($C_6H_{10}O_5)_n$

Glycogen is a polysaccharide of α -D-glucose. The carbohydrates are stored in animal body as **glycogen**. Just as glucose is stored in plants as starch, it is stored as glycogen in liver, muscles and brain of human beings. It serves as a **reserve carbohydrate**. When the body needs glucose during strenuous exercise or fasting, the enzymes break down glycogen to provide glucose. Glycogen is also present in yeast and fungi.

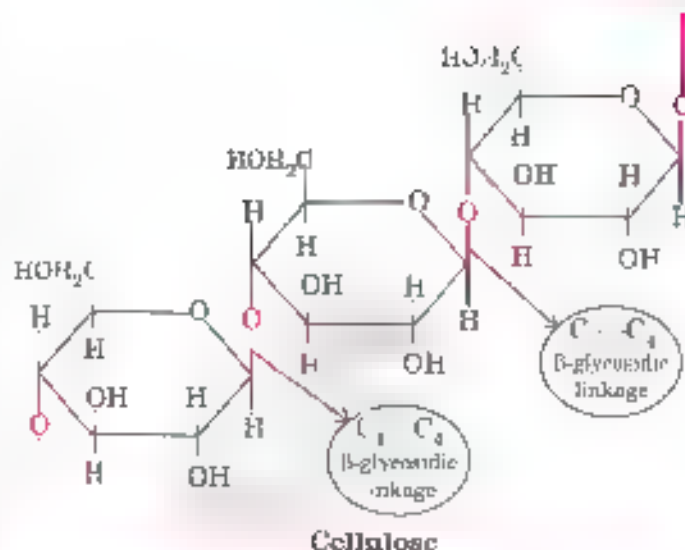
Structurally glycogen is a condensation polymer of α -D-glucose. It is known as **animal starch** because its structure is similar to **amylopectin**. The only difference between glycogen and amylopectin is that amylopectin chains consist of 20–25 glucose units but glycogen chains are shorter because they consist of 10–14 glucose units. Glycogen is more highly branched than amylopectin.

IMPORTANT FUNCTIONS OF CARBOHYDRATES

The important functions of carbohydrates are

1. Carbohydrates are essential for life in both plants and animals. They form a major portion of our food. Honey has been used for a long time as an instant source of energy by 'Vaid's' in ayurvedic system of medicine.

2. Carbohydrates, with the exception of cellulose, work as body fuels and act as the main **source of energy**. For example, slow oxidation of glucose by



C1 of one glucose unit is linked to C4 of next glucose unit.

A U Curious...

- ❑ **Why is cellulose not digestible?**
- The enzyme cellulase can hydrolyse cellulose into glucose and hence can digest cellulose. However human stomach does not have any enzyme capable of breaking cellulose molecules and therefore, cannot digest cellulose.

Molisch Test →

It is used for the detection of carbohydrates (monosaccharides, disaccharides or polysaccharides). To a 2 mL of aqueous carbohydrate solution in a test tube add 3–5 drops of alcoholic solution of 1% α -naphthol solution. Now add 1 mL of conc. sulphuric acid along the sides of the test tube. A **violet ring** is formed at the junction of two liquids. This is a general test for carbohydrates.

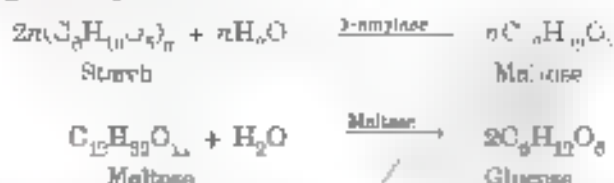
REMEMBER

- ATP is adenosine triphosphate.
- ATP is an energy rich molecule and acts as a **source of energy**.
- ATP acts as the centre of all activities of cell.
- During synthesis of 1 molecule of glucose in photosynthesis, 18 molecules of ATP are consumed.

a series of steps provides energy for living organisms



Polysaccharides first undergo hydrolysis to give glucose which then supplies the energy. Starch and sugars get hydrolysed to glucose by the enzymes present in the various juices secreted by different organs in the human and animal digestive systems.



3. The carbohydrates act as storage of energy for the functioning of living organisms. In case of emergency like famine & fasting, they supply energy. Starch is major food reserve in plants and glycogen in animals.

4. They form structural materials for cells. For example, cellulose is present in the cell walls of the plant cells.

5. Carbohydrates provide raw materials for many important industries such as textiles, papers, lacquers, breweries, etc.

6. The monosaccharides D-ribose and 2-deoxy-D-ribose are present in nucleic acids. These nucleic acids control the transmission of hereditary effects from one generation to another and also biosynthesis of proteins.

7. The monosaccharide ribose is an essential component of **adenosine triphosphate (ATP)** which acts as energy currency of the cells during metabolism of carbohydrates, proteins and fats. It is called **energy currency** of the cells because a part of chemical energy obtained by the oxidation of biomolecules such as carbohydrates, lipids, etc. is stored in the cells in the form of ATP which in turn carries out all the cellular functions.

RECURRING

1. Carbohydrates are reserve food materials.

- Starch is the major food reserve in plants. It is stored in seeds and acts as a reserve food material for tiny plants till they are capable of making their own food by photosynthesis. Similarly, glycogen stored in muscles and liver acts as the reserve food material in animals. In case of emergency caused by fasting or illness, the liver glycogen is readily hydrolysed to glucose, which is then gets oxidised in the blood to provide the much needed energy.

add on

Conceptual Questions 1

CONCEPTUAL

Q.1. Why are carbohydrates generally optically active?

Ans. Carbohydrates are generally optically active because they have one or more chiral carbon atoms.

Q.2. How do anomers differ from epimers?

Ans. Carbohydrates which differ in configuration at the glycosidic carbon (i.e. C_1 in aldoses and C_2 in ketoses) are called **anomers**. The carbohydrates which differ in configuration at any asymmetric carbon atom other than glycosidic carbon are called **epimers**. For example, α -D-glucose and β -D-glucose are anomers, differ at C_1 glycosidic carbon. On the other hand, glucose and mannose are epimers, differ in configuration at C_2 .

Q.3. What are the polysaccharides that make up starch and what is the difference between them?

Ans. Starch is a polymer of α -glucose. It consists of two components: amylose and amylopectin. Amylose is water soluble fraction and is a linear polymer of α -glucose. Amylopectin is water insoluble fraction which consists of branched chains of α -glucose.

Q.4. Is a diet consisting mainly of rice an adequate diet? Why or why not?

Ans. Adequate and good quality food is necessary for the physical and mental development. This food provides us energy for our daily work. Nutritious food should contain carbohydrates, fats, proteins and vitamins. Rice alone cannot supply these nutrients. Therefore, a diet mainly of rice is not adequate diet.

Q.5. Amylose and cellulose are both straight chain polysaccharides containing only D-glucose units. What is the structural difference between the two?

[N.C.E.R.T.]

Ans. Amylose is a straight chain polysaccharide having D-glucose units joined together by α -glycosidic linkages involving C_1 of one glucose unit and C_4 of the next glucose unit. On the other hand, cellulose is a straight chain polysaccharide having D-glucose units joined by β -glycosidic linkages between C_1 of one glucose unit and C_4 of the next glucose unit.

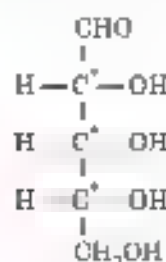
Q.6 What are reducing and non-reducing sugars? What is the structural feature characterising reducing sugars? (Meghalaya S.B. 2015)

Ans. Sugars which can reduce Tollen's reagent or Fehling's solution are called reducing sugars. The sugars which do not reduce Tollen's reagent or Fehling's solution are called non-reducing sugars.

The characteristic structural feature of reducing sugar is the presence of either α -hydroxy aldehyde group, $\text{H}-\text{C}(\text{H})-\text{OH}$, such as glucose, mannose, galactose, etc. or α -hydroxy keto group, $\text{C}(\text{H})=\text{C}(\text{H})-\text{OH}$ as present in fructose.

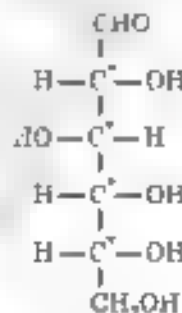
Q.7 Draw open chain structure of an aldopentose and aldohexose. Predict the number of asymmetric carbon atoms present in each.

Ans. The open chain structures of an aldopentose and aldohexose are



Aldopentose
D-(+)-Ribose

No. of asymmetric carbon atoms = 3



Aldohexose
D-(+)-Glucose

No. of asymmetric carbon atoms = 4

Q.8 What is meant by inversion of sugar?

(CBSE Sample Paper 2011, Pb. S.B. 2017)

Ans. The change of specific rotation of sugar from dextro rotatory to levo rotatory is called inversion of sugar.

Q.9 Glucose does not give 2, 4-DNP test and Schiff's test. Why?

(CBSE Sample Paper 2011)

Ans. Glucose has a cyclic structure in which H^+ group is not free because it forms a hemiacetal linkage with OH^- group at C_5 . Therefore, it does not give 2, 4-DNP test although it has H^+ group.

Q.10 Write any two reactions of glucose which could not be explained by open chain structure of glucose molecule. (D.S.B. 2019)

Ans. Open chain structure of glucose molecule cannot explain the following

(i) Glucose does not react with sodium bisulphite, NaHSO_3 , to form addition product though it has aldehyde group.

(ii) Glucose does not give Schiff's test and 2,4-DNP test like other aldehydes.

Q.11 Write a reaction which shows that all the carbon atoms in glucose are in a straight chain.

Ans. When glucose is heated with HI and red P at 150°C for a long period, it gives n-hexane and 2-iodohexane.



Glucose

n-Hexane

I

2-Iodohexane

The formation of n-hexane suggests that all the six carbon atoms in glucose are arranged in a straight chain.

Q.12 What is the name given to the linkage which holds together monosaccharide units in polysaccharides?

Ans. Glycosidic linkage.

Q.13 Give one example each of disaccharide and polysaccharide.

(Jharkhand S.B. 2018)

Ans. Disaccharide: Sucrose, $\text{C}_{12}\text{H}_{22}\text{O}_{11}$

Polysaccharide: Starch, $(\text{C}_6\text{H}_{10}\text{O}_5)_n$

Q.14 What are the products of hydrolysis of sucrose?

(Hr. S.B. 2012, Assam S.B. 2012, A.I.S.B. 2014)

Ans. Glucose and fructose

Q.15 What are the products of hydrolysis of lactose?

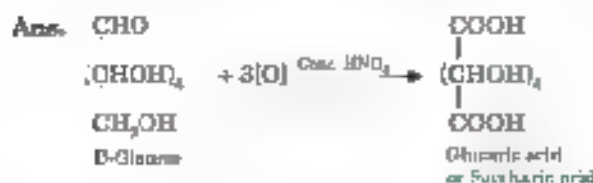
(Hr. S.B. 2012, A.I.S.B. 2014)

Ans. Glucose and galactose

Q.16 Name the disaccharide present in milk.

Ans. Lactose.

Q.17 Write the product when D-glucose reacts with conc. HNO_3 .
(A.I.S.B. 2018)



PROTEINS

Proteins are **high molecular mass complex biomolecules of amino acids present in all living cells**. The chief source of proteins are milk, cheese, pulses, peanuts, fish meat, etc. They occur in every part of the body and form the **fundamental basis of structure and functions of life**. The name **proteins** is derived from the Greek word **protein** which means **primary or of prime importance**. These are so named because proteins are **vitally chemical substances essential for growth and maintenance of life**. They are present almost in all the living cells of plants and animals. The protoplasm of plant or animal cells contains 10–20% proteins. The important proteins required for our body are

- **enzymes** as biocatalysts to catalyse biochemical reactions,
- **hormones** to regulate various body functions,
- **antibodies** to protect the body against toxic substances and infections,
- **transport proteins** to carry different substances in the blood to various tissues of the body
- **structural proteins**, structural elements of the cells and tissues,
- **contractile proteins** like in the contraction of muscles and other cells etc.

All proteins contain the elements carbon, hydrogen, oxygen, nitrogen and sulphur. Some of these may also contain phosphorus, iodine and traces of metals such as iron, copper, zinc, manganese, etc.

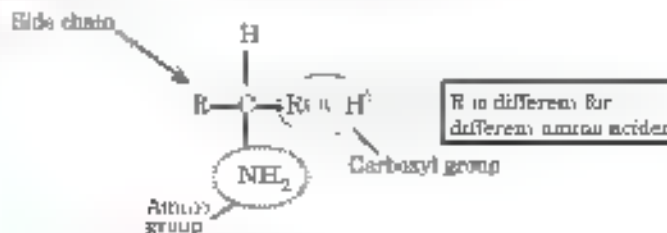
All proteins on partial hydrolysis give peptides of varying molecular masses which on complete hydrolysis give α -amino acids.



Thus, chemically proteins are **condensation polymers (polyamides)** in which the **monomer units are α -amino acids**.

AMINO ACIDS

α -Amino acids are building blocks of proteins. **Amino acids are organic compounds containing both an amino group and carboxyl group**. They are represented by the general formula



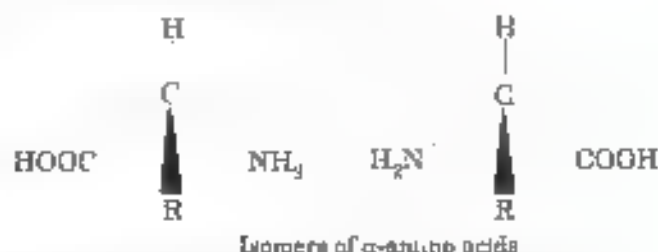
The amino (NH_2) group may be attached to any carbon atom other than that of carboxyl (COOH) group. They are referred to as α , β , γ depending upon whether the amino group is present on α , β or γ carbon atom relative to carboxyl group. Nearly all the naturally occurring amino acids are α -amino acids, i.e., containing amino group on the α (adjacent) carbon atom to carboxyl group. The general structure of α -amino acid is shown above. These amino acids are very important because these are the building blocks of proteins which are very essential for us.

REMEMBER

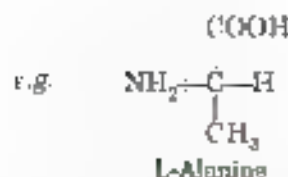
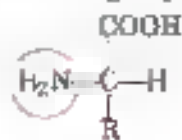
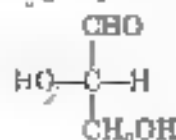
- If the NH_2 group at the chiral carbon lies on the left hand side as in L-(+)-glyceraldehyde, the amino acid belongs to L-series and
- if it is towards right as in D-(-)-glyceraldehyde it is said to belong to D-series.

L-Family of Amino Acids

With the exception of glycine, all other α -amino acids have chiral carbon atom and have two optically active isomers.



However all naturally occurring amino acids belong to L-series which have NH_2 group on the left as OH group in L-glyceraldehyde

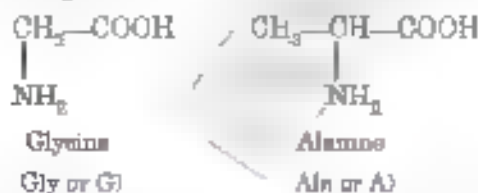


—NH_2 group is on the left hand side as —OH is in glyceraldehyde

Nomenclature of Amino Acids

Although amino acids can be named according to IUPAC system, they are generally known by their common names or trivial names. For example $\text{NH}_2\text{CH}_2\text{COOH}$ is better known as glycine rather than α -amino acetic acid or 2-amino ethanoic acid. The trivial names are derived either from the name of the source or the name of some characteristic property of that amino acid. For example, glycine is so named because it has sweet taste in greek *glykos* means sweet and tyrosine was first obtained from cheese in greek *tyros* means cheese.

For the sake of simplicity each amino acid has been given an abbreviation which generally consists of the first three letters or one letter symbols of its common name. For example α -amino acid is glycine $\text{NH}_2\text{CH}_2\text{COOH}$. It may be abbreviated as Gly. Sometimes one letter symbols are also used. For example, glycine is represented by G. Similarly alanine $\text{CH}_3\text{CH}(\text{NH}_2)\text{COOH}$ may be represented as Ala or A.



Classification of α -Amino acids—Neutral, acidic or basic amino acids

Amino acids can be broadly classified as **acidic**, **basic**, or **neutral amino acids** depending upon the relative number of amino and carboxyl groups in their molecules.

Neutral amino acids contain equal number of amino and carboxyl groups. For example, amino acids such as glycine, alanine, valine etc. are neutral amino acids.

Acidic amino acids contain more number of carboxyl groups than amino groups. For example, aspartic acid, glutamic acid which contain two COOH groups and one NH_2 group are acidic amino acids.

Evidence for the Existence of Dipolar Ions. The following facts support the existence of dipolar ions both in the solid form and in aqueous solutions of amino acids.

(i) Amino acids are non-volatile crystalline solids with fairly high melting points. For example, glycine has m.p. of 262°C . The high melting points of amino acids suggest large intermolecular forces in the crystals which are due to the electrostatic interactions of the dipolar ions.

(ii) Aqueous solutions of amino acids behave like solutions of substances having high dipole moments.

(iii) Like ionic compounds, they are insoluble in non-polar organic solvents like benzene, petroleum ether or ether but are highly soluble in polar solvents like water.

(iv) Acidity and basicity constants are very low for COOH and NH_2 group. For example, glycine has $K_a = 1.6 \times 10^{-10}$ and $K_b = 2.6 \times 10^{-10}$ whereas most carboxylic acids have K_a values of about 10^{-5} and most aliphatic amines have K_b values of about 10^{-4} . This is because in α -amino acids, NH_2 group acts as an acid and COOH group acts as the base.

(v) Spectroscopic studies of these amino acids do not show the presence of free —OH and free —NH groups.

(vi) Examination of glycine crystals by X-rays shows that it has the structure $\text{NH}_3^+\text{CH}_2\text{COO}^-$ in the solid state.

All above facts support that amino acids have dipolar ion structure.

Basic amino acids contain more number of amino groups than carboxyl groups. For example, *lysine*, *arginine*, and *histidine* which contain two NH_2 groups and one COOH groups are basic amino acids.

The structures of 20 amino acids are given in Table 2 ahead.

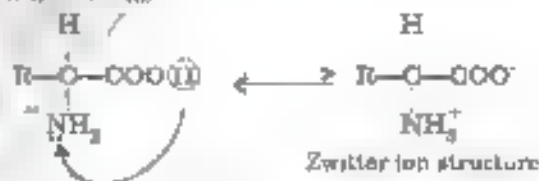
Essential and non-essential amino acids

Certain amino acids can be made by our bodies and, therefore, we do not require them in our diet. These are called **non-essential amino acids**. The human body can synthesise 10 out of 20 amino acids found in proteins. Therefore, other must be supplied in our diet and these are called **essential amino acids**. The 10 essential amino acids are valine, leucine, isoleucine, arginine, lysine, threonine, methionine, phenylalanine, tryptophan, and histidine. These essential amino acids are required for the growth of our body and lack of these essential amino acids in diet can cause diseases such as *Kwashiorkor*.

PROPERTIES AND STRUCTURE OF AMINO ACIDS

Physical Properties of α -Amino acids

Amino acids are usually colourless, crystalline solids. These are soluble in water and have high melting points. Therefore, they behave like salts rather than simple amines or carboxylic acids. This behaviour is due to the presence of both acidic and amino groups in the same molecule. Therefore, the amino acid exists as *dipolar ion* called a **zwitter ion**. It has positive as well as negative ends within the same molecule. In the formation of zwitter ion, the proton goes from the carboxyl group to the amino group. The zwitter ion structure of α -amino acid may be written as

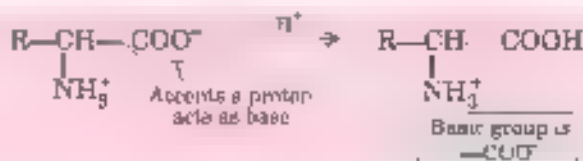


The zwitter structure is also called **internal salt**. All α -amino acids exist largely in dipolar ionic forms.

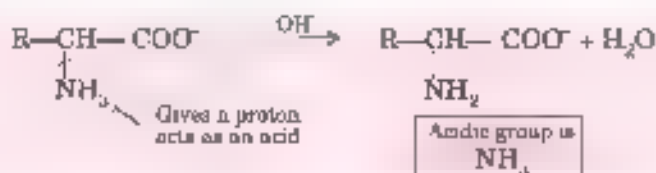
Acidic and basic character of amino acids according to dipolar ion structure:

On the basis of dipolar ion structure, the acidic and basic reactions of amino acids may be represented as

1. When the solution of amino acid is made acidic or an acid is added to amino acid, COO^- accepts the proton and gets converted to carboxyl substituent (COOH). Therefore, the **basic character is due to COO^- group**.



When an alkali is added to amino acid, NH_3^+ group releases the proton and changes to amino NH_2 group. Therefore, the **acidic character is due to NH_3^+ group**.



Essential Amino acids

- Valine
- Leucine
- Isoleucine
- Arginine
- Lysine
- Threonine
- Methionine
- Phenylalanine
- Tryptophan
- Histidine

These essential amino acids are required for the growth of our body and their deficiency causes diseases such as *Kwashiorkor*. In this disease, water balance in the body is disturbed. As a result, some organs of the body become watery and bloated.

REMEMBER

In α -amino acids

- acidic character is due to NH_3^+ group
- basic character is due to COO^- group

Thus, in amino acids, the basic character is due to the -COO^- group whereas the acidic character is due to the -NH_3^+ group.

Table 2 Structures and names of some α -amino acids having general structure :

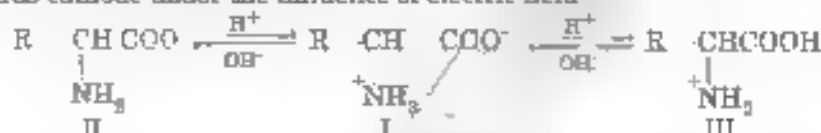


α -amino acid	R Group	Three letter Abbreviation	One letter Abbreviation
<u>Neutral Amino Acids</u>			
1. Glycine	H	Gly	G
2. Alanine	-CH_3	Ala	A
3. Valine*	$\text{-CH}(\text{CH}_3)_2$	Val	V
4. Leucine*	$\text{-CH}_2\text{-CH}(\text{CH}_3)_2$	Leu	L
5. Isoleucine*	$\text{-CH}(\text{CH}_3)\text{-CH}_2\text{-CH}_3$	Ile	I
6. Phenylalanine*	$\text{-CH}_2\text{-Ph}$	Phe	F
7. Methionine*	$\text{-CH}_2\text{-CH}_2\text{-S-CH}_3$	Met	M
8. Tryptophan*	$\text{-CH}_2\text{-}$ 	Trp	W
9. Proline	 H (Complete structure)	Pro	P
10. Serine	$\text{-CH}_2\text{-OH}$	Ser	S
11. Cysteine	$\text{-CH}_2\text{-SH}$	Cys	C
12. Asparagine	$\text{-CH}_2\text{-CONH}_2$	Asn	N
13. Glutamine	$\text{-CH}_2\text{-CH}_2\text{-CONH}_2$	Gln	Q
14. Threonine*	$\text{-CH}(\text{OH})\text{-CH}_3$	Thr	T
15. Tyrosine	$\text{-CH}_2\text{-}$  OH	Tyr	Y
<u>Acidic Amino Acids</u>			
16. Aspartic acid	$\text{-CH}_2\text{-COOH}$	Asp	D
17. Glutamic acid	$\text{-CH}_2\text{-CH}_2\text{-COOH}$	Glu	E
<u>Basic Amino Acids</u>			
18. Lysine*	$\text{-CH}_2\text{-(CH}_2\text{)}_4\text{-NH}_2$	Lys	K
19. Arginine*	$\text{-CH}_2\text{-(CH}_2\text{)}_3\text{-NH-C(=NH)-NH}_2$	Arg	R
20. Histidine*	$\text{-CH}_2\text{-}$ 	His	H

* Coloured are essential amino acids. Ph stands for phenyl

Ninhydrin test. All amino acids on treatment with ninhydrin (2,2-dihydroxyindane-1,3-dione) give purple colouration. This test is called **ninhydrin test** and is used for the detection of amino acids.

Amino acids have zwitter ion structure, $\text{NH}_3^+\text{CH(R)COO}^-$ and we expect that their aqueous solutions would be neutral. However aqueous solutions of neutral amino acids are slightly acidic because the acidic character of NH_3^+ group is more than the basic character of COO^- groups. When we place the aqueous solution of an amino acid in an electric field, its behaviour will depend upon the acidity or basicity of the solution. In alkaline solution, an amino acid exists as a negative ion, II and migrates towards anode under the influence of electric field. On the other hand, in acidic solution, it exists as a positive ion, III and migrates towards cathode under the influence of electric field.

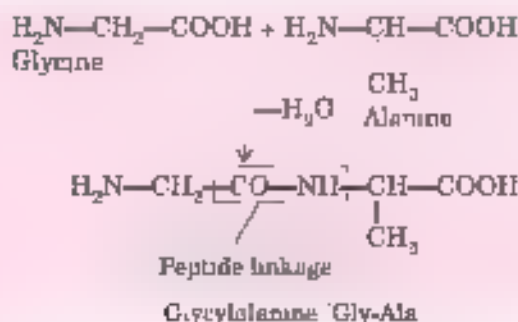


The pH or hydrogen ions concentration of the solution at which a particular amino acid does not migrate under the influence of an electric field is called **isoelectric point** of that amino acid.

At constant pH point, the amino acids have the least solubility in water and this property is used for the separation of different amino acids obtained from the hydrolysis of proteins.

PEPTIDES AND PROTEINS

The formation of a **dipeptide** and the peptide linkage is shown below:

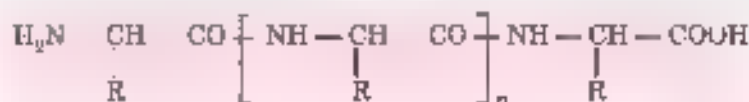


Alternatively the amino group of glycine may react with carboxyl group of alanine resulting in the formation of a different dipeptide, α -alanyl-glycine, Ala-Gly. In both these dipeptides, i.e. glycyl-alanine or α -alanyl-glycine there are free functional groups at both ends. These groups can further react with the appropriate groups of other amino acids forming tri-, tetra- pentapeptides and so on.

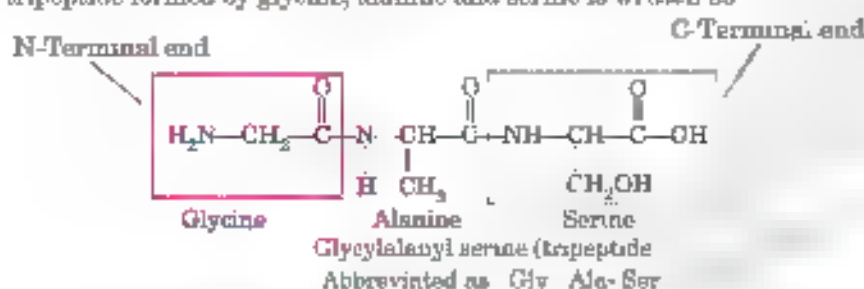
$\text{C}=\text{NH}-$ bond is called
peptide bond or peptide linkage.

Polypeptides

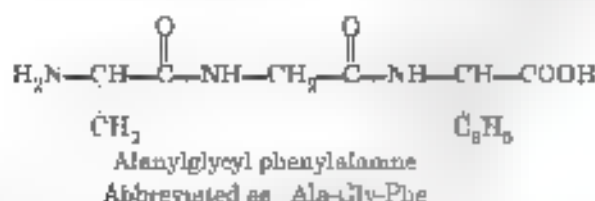
If a large number of α -amino acids (hundreds to thousands) are joined by peptide bonds, the resulting polyamide is called **polypeptide** as shown below



It is clear from the above structure that each polypeptide chain has a *free amino group* (NH_2) at one end and the *free carboxyl group* (COOH) at the other end. The amino group end is called amino or **N-terminal** end while the end having free COOH group is called **C-terminal end**. The structure is generally written with N-terminal end to the left and C-terminal end to the right. The name of the peptide is written from the names of the amino acids as they appear from left to right, starting from N-terminal amino acid. The suffix **-one** in the name of the amino acid is replaced by **-yl** as glycine to glycyl, alanine to alanyl, etc. for all amino acids except C-terminal acid. Generally polypeptides are written with three letter abbreviation or one letter abbreviation for amino acids. For example the tripeptide formed by glycine, alanine and serine is written as



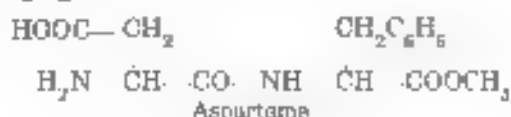
Similarly a tripeptide alanylglycyl-phenylalanine is represented as



Depending upon the number of amino acids residues per molecule the peptides are called *dipeptide*, *tripeptide*, *polypeptide*, etc. The formation of peptide bonds can continue until a molecule containing several hundred thousands amino acids is formed. Relatively shorter peptides are called **oligopeptides**, while larger polymers are called **polypeptides** or **proteins**. By convention, a *peptide* having molecular mass upto $10,000 \text{ u}$ is called **polypeptide**, while a *peptide* having a molecular mass more than $10,000 \text{ u}$ is called a **protein**. However the distinction between a polypeptide and a protein is not very sharp. A polypeptide with a fewer α -amino acids may also be called a protein if it has a well defined conformation of a protein, such as insulin which contains 51 amino acids.

Polypeptides are *amphoteric* because of the presence of terminal ammonium and carboxylate ions as well as the ionized side chains of amino acid residues. Therefore they behave as acids or bases and have an isoelectric point at which they are frequently least soluble and have the greatest tendency to aggregate.

Most of the toxins/poisonous substances in animal venoms and in plant sources are polypeptides. A derivative of dipeptide aspartyl phenylalanine methyl ester, aspartame, is about 100 times as sweet as sucrose and is used as sugar substitute as sweetening agent.



REMEMBER

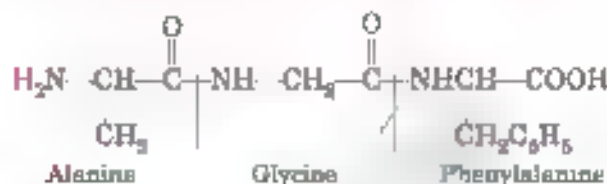
Insulin protein contains 51 amino acids

SOLVED EXAMPLES

□ Example 1

Write the formula of a tripeptide alanylglycyl phenylalanine

Solution : The formula of tripeptide is



□ Example 2

A tripeptide on complete hydrolysis gives valine, alanine and phenylalanine. Using three letter symbols write down the possible sequences of the tripeptide

Solution : The possible combinations are

- | | | |
|------------------|------------------|-------------------|
| (i) Gly-Ala-Phe | (ii) Ala-Gly-Phe | (iii) Phe-Gly-Ala |
| (iv) Gly-Phe-Ala | (v) Ala-Phe-Gly | (vi) Phe-Ala-Gly |

PROTEINS

Proteins are complex nitrogenous molecules which are essential for the growth and maintenance of life. These perform a wide variety of biological functions. Proteins are the constituents of cells and, therefore, are present in all living bodies. The molecular masses of proteins are very high. **Structurally, proteins are long polymers of amino acids linked by peptide (C=O, N-H) bonds.**

H

CLASSIFICATION OF PROTEINS

A Classification of proteins on the basis of molecular structure

Proteins can be classified into two broad classes on the basis of molecular structure as

(i) Fibrous proteins (ii) Globular proteins

(i) Fibrous proteins. These types of proteins consist of *linear thread like structures which tend to tie side by side to form fibres*. The molecules are held together at many points by hydrogen bonds or disulphide bonds. These are usually *insoluble in water*. The common examples of fibrous proteins are *keratin in skin, hair, nails and wool, collagen in tendons, fibroin in silk, myosin in muscle*, etc. These proteins serve as the main structural materials of animal tissues.

(ii) Globular proteins. In this type of proteins, *the molecules are folded together into compact units form e.g. spheroidal shapes*. The peptide chains in globular proteins are also held by hydrogen bonds but these forces are comparatively weak. These are *soluble in water or aqueous solutions of acids, bases or salts*. The common examples of globular proteins are *albumin, insulin*, etc.

The globular proteins have many important biological functions. For example,

- Some biological proteins function as enzymes to catalyse biological reactions.

Some proteins regulate metabolic reactions. For example, the protein hormone *insulin* (from pancreas) maintains blood sugar level.

• Some proteins act as antibodies which protect the body from allergies and provide defence against foreign organisms.

Differences between globular and fibrous proteins

Globular proteins	Fibrous proteins
1. These proteins are cross linked condensation products of basic and acidic amino acids	These are linear condensation products
2. These are soluble in water or aqueous solutions of acids, bases or salts.	These are insoluble in common solvents but soluble in strong acids and bases
3. The globular protein molecules are folded to give three dimensional, spheroidal shapes. These are stabilised by various hydrogen bonds	The long linear protein chains are held together by intermolecular hydrogen bonds.
4. Examples of globular proteins are albumins in egg, all enzymes and haemoglobin	Example are myosin in muscles, keratin in hair, fibrous in silk, collagen in tendons

Classification of proteins on the basis of hydrolysis products

Based on the type of products formed on hydrolysis, the proteins may be classified as

- (i) *Simple proteins* (ii) *Conjugated proteins* (iii) *Derived proteins*.

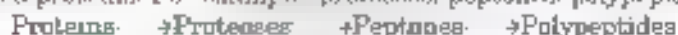
Simple proteins. These are proteins which give amino acids only on hydrolysis with acids or enzymes. The important examples are *albumins, globulins, glutalins, prolamines, keratin*, etc.

(i) **Conjugated proteins.** These are proteins which on hydrolysis give a non-protein part and α -amino acids. That is, these are formed by the combination of simple proteins with some non-proteinous substance. The non-proteinous part is called **prosthetic group** and it controls the biological functions of the protein. The common prosthetic groups in the proteins are

Name of proteins	Prosthetic group
Nucleo proteins	Nucleic acids
Glyco proteins	Sugars, carbohydrates
Lipo proteins	Lipids such as leucides
Phospho proteins	Phosphoric acid residues
Chromo proteins	Pigment having some metals
Haemoglobin and myoglobin	such as Fe, Cu (Haemoglobin)

The most important are the phosphorus containing nucleo proteins. They are compounds of simple proteins and nucleic acid and are found in cell nuclei.

(ii) **Derived Proteins.** They are the products of partial hydrolysis of simple or conjugated proteins. For example, proteoses, peptones, polypeptides, etc.



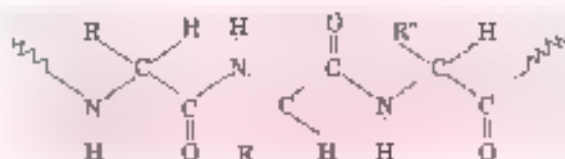
STRUCTURE OF PROTEINS

Proteins are macromolecules containing a large number of amino acids joined together through peptide bonds having three dimensional (3D) structures.

The structure of proteins is very complex. The protein structure and all type can be usually studied at four different levels i.e. *primary secondary tertiary and quaternary structures*. These are discussed as follows

1. Primary structure

Proteins may have one or more polypeptide chains. Each polypeptide in a protein has amino acids linked with each other in a specific sequence. This sequence of amino acids is said to be the primary structure of that protein. **Thus, the sequence in which the amino acids are linked in one or more polypeptide chains of a protein** is called the **primary structure** of protein as shown below



The primary structure is usually determined by its successive hydrolysis with enzymes or mineral acids. The amino acid sequence of a protein determines its function and is critical to its biological activity. *Frederick Sanger* determined the primary structure of a protein, *insulin*, for the first time in 1953. The importance of primary structure of a protein lies in the fact that even a change of one amino acid can change drastically the properties of the entire protein. It also creates a different protein. For example, a normal haemoglobin has 574 amino acid units and changing just one amino acid in the sequence results in defective haemoglobin found in patients suffering from *sickle cell anaemia*.

Normal haemoglobin

Val—His—Leu—Thr—Pro—Glu—Val—Lys—

Sickle cell haemoglobin

Val—His—Leu—Thr—Pro—Val—Glu—Lys—

In the patients suffering from sickle cell anaemia, the defective haemoglobin in red blood cells precipitates causing the cells to sickle and sometimes even burst leading ultimately to the death.

A protein containing a total of 101 amino acid residues is a very small protein, yet 20 different amino acids can be combined at one time in 20^{101} different ways.

2. Secondary structure

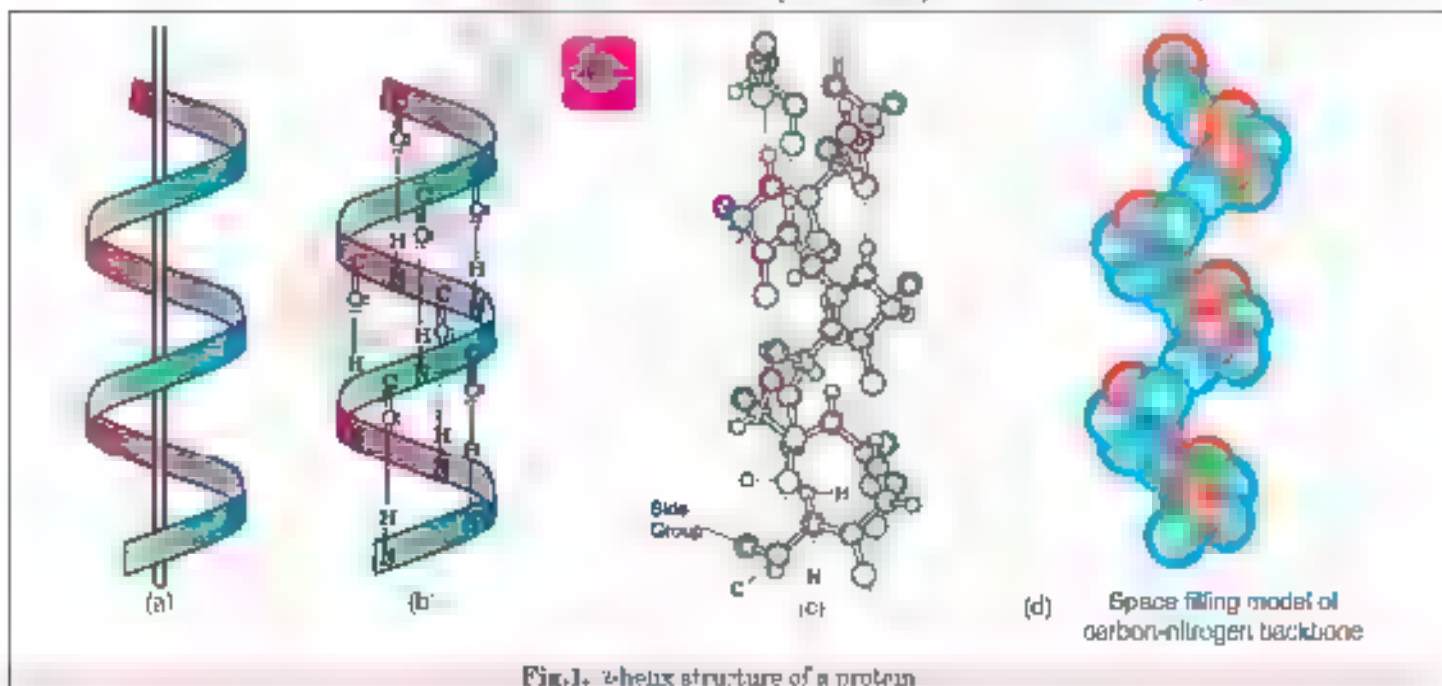
The secondary structure gives the manner in which the polypeptide chains are folded or arranged. Therefore, it gives the *shape or conformation of the protein molecule*.

This arises from the planar geometry of the peptide bond and hydrogen bond between the $>C=O$ and $N-H$ groups of different peptide bonds.

Pearson and Corey gave the structures of many proteins with the help of X-rays patterns. It was observed that there are two common types of structures.

α -Helix structure

It is the most common form in which a polypeptide chain forms all possible types of hydrogen bonds by twisting into a right handed screw helix with the $-NH$ group of each amino acid residue hydrogen bonded to the $>C=O$ group of an adjacent turn of the helix as shown in Fig. 1.6. This is called α -helix. This structure can be imagined as if one can coil a polypeptide chain around an invisible cylinder. The α -helix model was proposed by *Linus Pauling* in 1951 on the basis of theoretical considerations. However, it was later verified experimentally. To understand this, let us consider the



geometry of peptide bond. A peptide bond is shown below in this structure. The peptide groups are trans to each other.

The carbon-oxygen bond in the amide linkage is usually short which indicates the resonance between the two structures.



Due to the partial double bond character of the C-N bond in peptide linkage the amide part i.e. $\text{NH}-\text{C}(=\text{O})$ is planar and rigid. Therefore, rotation of groups about this bond is not possible. As a result of hindered rotation the peptide bond can show geometrical isomerism i.e. *cis*- and *trans*-forms. Further because of much larger steric repulsions between the alkyl groups, the *cis*-form is not stable. The *trans*-form is more stable and therefore, the peptide groups are trans to each other.

However, rotation of a peptide chain can occur only around the bonds joining the nearly planar amide groups to the carbonyl carbon α -carbon.

These rotations allow peptide chains to form different conformations. The angles through which rotations are possible are also called the *torsion angles* after the name of the Indian Biophysicist G.N.A. Ramachandran. They were defined in terms of angle ϕ for α -carbon to amide nitrogen bond i.e. between $\text{R}_1-\text{CH}-\text{NH}$ and angle ψ for the α -carbon to a carbonyl bond i.e. between $\text{R}-\text{CH}-\text{C}(=\text{O})$.

The stability of the structure is due to the hydrogen bonding between NH and $\text{C}(=\text{O})$ groups of peptide bonds. Therefore, a structure having maximum hydrogen bonding shall be stable and favoured. The α -helix structure is also known as 3.6_{13} helix. This represents that each turn of the helix contains approximately 3.6 amino acids and a 13-member ring is formed by hydrogen bonding. The helix is held in its shape primarily by hydrogen bonds between one amide group's carbonyl group which is 4.0 or more amino acids away.

It may be noted that in proteins, the helix has always a right handed arrangement. If you keep your hand so that the thumb points in the direction of travel along the axis of the helix, then the curl of your fingers gives the direction in which the helix rotates. All amino acids in a polypeptide chain have L-configuration and therefore it can form a stable α -helix only if it is right handed. α -helix structure is found in many proteins such as *myosin* (found in muscles) and *keratin* (found in hair, wool and nails).

(ii) β -pleated sheet structure

This was also proposed by Linus Pauling and co-workers in 1951. In this structure, a polypeptide chains are stretched out to nearly maximum extension and then laid side by side in a zig-zag manner to form a flat sheet. Each chain is held to the two neighbouring chains by **hydrogen bonds**. These sheets are stacked one upon another to form a three dimensional structure called β -pleated sheet structure (Fig. 2). The structure resembles the pleated folds of drapery and, therefore, is known as β -pleated sheet.

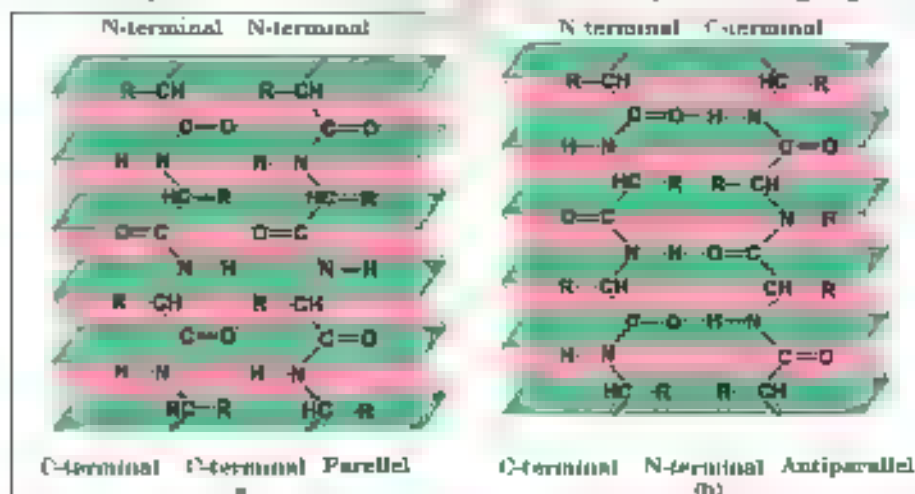


Fig. 2. β -sheet, pleated structure of a protein.

Two types of pleated sheets are possible. The polypeptide chains may run parallel i.e. the adjacent chains run in the same direction or may be antiparallel i.e. the adjacent chains run in the opposite direction as shown in Fig. 2. In other words, in parallel β -conformation N-termini are aligned head to head i.e., on the same side. On the other hand, in antiparallel conformation [Fig. 2 (b)] the polypeptide chains are aligned head to tail which means that N-terminus of one chain and

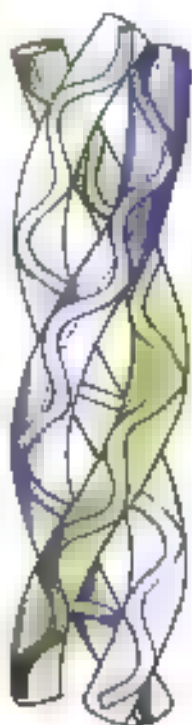


Fig. 3. Triplex helix structure of collagen.

C-terminus of another chain are on the same side. For example, *keratin proteins* in hair has parallel β -sheet structure and *skin protein fibronin* has antiparallel β -sheet structure.

It may be noted that a protein may or may not have the same secondary structure throughout its length. Some parts of the chain may have α -helix structure while other parts may have β -pleated sheet structure. Some parts of the chain may even have no secondary structure at all. Such a **structureless part** is called a **random coil**.

3. Tertiary structure

The **tertiary structure** arises due to **folding, coiling and bending** of polypeptide chains producing **three-dimensional structures**. This structure gives the **overall shape of proteins**. In other words, the tertiary structure of a protein gives the overall folding of polypeptide chains i.e. further folding of the secondary structure. Two major molecular shapes found are fibrous and globular. These are already discussed.

The **fibrous proteins** such as **skin collagen** and **co-keratins** have large water content and have rod-like rigid shape and are insoluble in water. The structure of collagen triple helix is shown in Fig. 3.

In the other hand, in **globular proteins** such as **haemoglobin** the polypeptide chains consist partly of helical sections which are folded about the random coils to give it a spherical shape. Perutz and Kendrew determined the tertiary structure of haemoglobin and myoglobin through X-rays determination and were awarded Noble Prize in 1962.

The main forces which stabilise the secondary and tertiary structures of proteins are hydrogen bonds, sulphide linkages, van der Waals and electrostatic forces of attraction.

4. Quaternary Structure

Many proteins exist as a single polypeptide chain but there are some proteins which exist as assemblies of two or more polypeptide chains called **sub-units** or **protomers**. These sub-units may be identical or different. These are held together by non-covalent forces

such as hydrogen bonds, electrostatic interactions and van der Waals interactions. The **quaternary structure** refers to the determination of the number of sub-units and their arrangement in an aggregate protein molecule. The best known example of a protein possessing quaternary structure is **haemoglobin** which transports oxygen from the lungs of the cells and carbon dioxide from the cells to the lungs through the blood stream. It is an aggregate of four polypeptide chains or sub-units, two identical α chains each containing 141 amino acid residues and two identical β chains each containing 146 amino acid residues. These four sub-units lie more or less at the vertices of a regular tetrahedron. Each polypeptide chain carries a heme group (iron-protoporphyrin complex) at its end.

The four types of structures of proteins are shown in Fig. 4. In this structure each ball represents an amino acid.

The primary, secondary, tertiary and quaternary structures of haemoglobin are shown in Fig. 5.

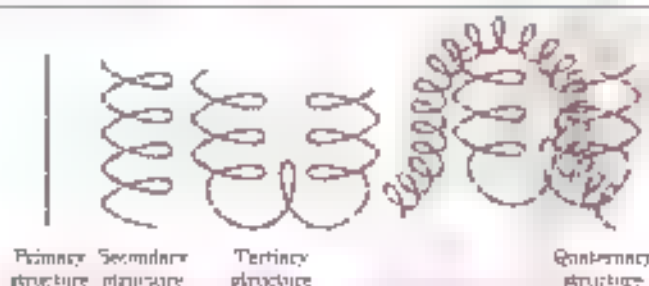


Fig. 4. Diagrammatic representation of protein structure: two sub-units of two types in quaternary structure

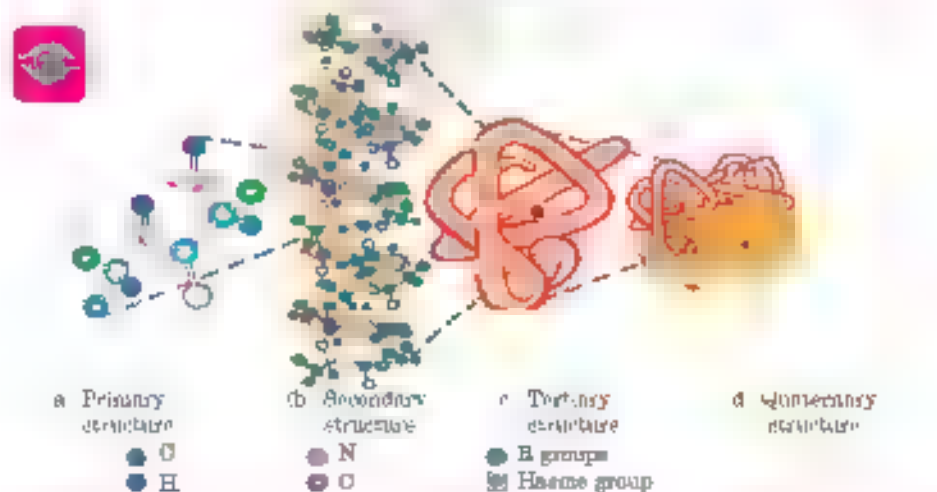


Fig. 5. Primary, secondary, tertiary and quaternary structures of haemoglobin

FORCES THAT STABILIZE PROTEIN STRUCTURES

The following types of forces stabilize the protein structure

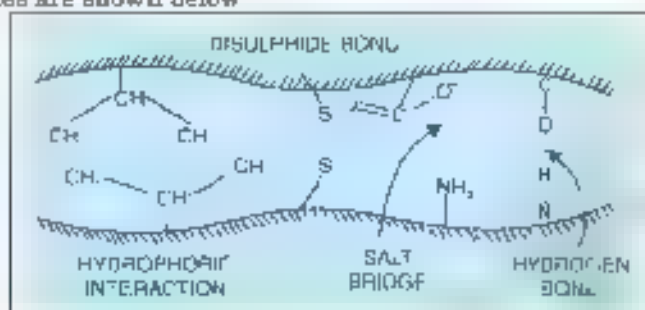
1. Hydrogen bonding. These are weak forces and arise between a partially positive hydrogen and a partially negative atom such as oxygen, fluorine or nitrogen on the same or different molecule.

2. Ionic bonding. Ionic bonding can take place between an ionic and cationic side chains resulting side chain cross linking.

3. Covalent bonding. The most common form of inter-chain bonding is the disulphide bond formed between the sulphur atoms of two cysteine residues. The insulin consists of two polypeptide chains linked together by covalent bonding.

4. Hydrophobic bonding. Many amino acid residues have hydrophobic water-hating side chains. Proteins in aqueous solutions fold so that most of the hydrophobic chains become clustered inside the folds. The polar side chains which are hydrophilic water-loving are on the outside or the surface of the protein.

These forces are shown below



NATIVE STATE AND DENATURATION OF PROTEINS

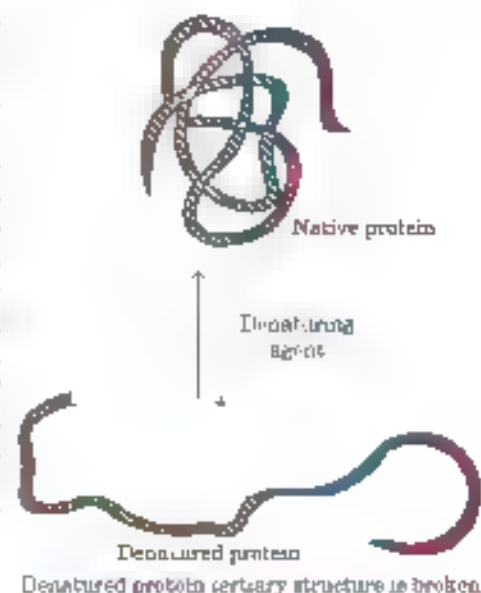
Native state. The most energetically stable state of a protein is called its **native state**. In other words, native state corresponds to the protein's form in a biological system with a unique three dimensional structure or configuration and biological activity.

Denaturation of proteins. A process that changes the physical and biological properties of proteins without affecting the chemical composition of a protein is called **denaturation**. The denaturation is caused by certain physical change like change in temperature or a chemical change like change in pH, presence of salts or certain chemical agents. Due to this globules unfold and helix get uncoiled. As a result, the protein molecule uncoils from an ordered and specific conformation into a more random conformation and protein precipitates from solution. Changes in pH have the greatest disruptive effect on hydrogen bonding and salt bridges in proteins. For example, the polypeptide polylysine is composed of amino acid lysine molecules which have amino acid group in the side of the chain. In acidic medium, all side chains get protonated and become positively charged. As a result of similar charge they repel each other and causing the molecule to uncoil. Heating increases the thermal vibration of the molecule, disrupting hydrogen bonding and salt bridges. The denatured proteins will lose its biological activity. It may be noted that during denaturation the secondary and tertiary structures are destroyed but the primary structure remains intact.

Protein denaturation may or may not be reversible.

Examples of Denaturation of Proteins

1. The most common example of denaturation of proteins is the coagulation of albumin present in the white of an egg. Proteins present in egg white are



REMEMBER

Denaturation does not change the primary structure of proteins.

globular and soluble. When an egg is boiled in water, the globular proteins present in it change to a rubber like *insoluble mass*. Thus, is **irreversible denaturation** and the protein cannot return to its original state.

2. Curdling of milk is another example of denaturation of proteins. It is caused due to the formation of lactic acid by the bacteria present in milk.

3. The coagulation of milk in the presence of an acid (lemon juice) to form *cheese* is also an example of denaturation of proteins. During this denaturation, the globular milk protein lactalbumin becomes fibrous.

It may be noted that in some cases, the denaturation process is reversible. It is found that if the disruptive agent is removed, the protein recovers its original physical and chemical properties and biological activity. The reverse process of denaturation is called **renaturation**.

ENZYMES

The **enzymes** are biological catalysts produced by living cells which catalyse the biochemical reactions in living organisms. Chemically, enzymes are naturally occurring simple or conjugate proteins. Some enzymes may be non-proteins also. Almost all enzymes are globular proteins. Without enzymes, the living processes would be very slow to sustain life. For example, without the presence of enzymes in our digestive tract, it would take about 50 years to digest a single meal. All enzymes are proteins. About 3000 enzymes have been identified. The enzymes differ from other types of catalysts in being *highly selective and specific*.

The enzymes are generally named after the compound or class of compound upon which they work. For example, the enzyme which catalyses the hydrolysis of maltose into glucose is named as **maltase**.



Sometimes the enzymes are also named after the reaction where they are used. For example, the enzymes which catalyse the oxidation of one substrate with simultaneous reduction of another substrate are named as **oxidoreductase enzymes**. The ending of the name of an enzyme is **-ase**.

The enzymes facilitates the biochemical reactions by providing alternative lower activation energy path and, therefore, increases the rate of reactions. At present about 3000 enzymes have been recognized by the International Union of Biochemistry. However, only about 10% i.e. 300 are commercially available. Some common enzymes and the reactions which are catalysed by them are given in Table 3.

Table 3: Some common examples of enzymes.

Enzyme	Reaction catalysed	
Maltase	Maltose	→ Glucose + Glucose
Lactase	Lactose	→ Glucose + Galactose
Amylase	Starch	→ n × Glucose
Invertase	Sucrose	→ Glucose + Fructose
Urease	Urea	→ $\text{CO}_2 + \text{NH}_3$
Carbonic anhydrase	H_2CO_3	→ $\text{CO}_2 + \text{H}_2\text{O}$
Pepsin	Proteins	→ Amino acids
Trypsin	Proteins	→ Amino acids
Nucleases	DNA, RNA	Nucleotides
RNA Polymerase	Ribonucleotide triphosphates	→ RNA
DNA Polymerase	Deoxyribonucleotide triphosphates	→ DNA

Properties of Enzymes

The important characteristics of enzymes are

1. **High efficiency** Enzymes increase the speed of reactions up to 10^{10} times as compared to the uncatalysed reactions. This is because the enzyme reduces the magnitude of activation energy. For example, the activation energy of acid hydrolysis of sucrose is 6.22 kJ mol^{-1} while the activation energy is only 2.15 kJ mol^{-1} when hydrolysis is carried out by the enzyme *sucrase*.

2. **Extremely small quantities** Extremely small quantities of enzymes, as small as millionth of a mole—can increase the rate of reaction, by factors of 10^4 to 10^6 .

3. **Specificity** The enzymes are highly specific in nature. Almost every biochemical reaction is controlled by its own specific enzymes. For example, *maltase* catalyses the hydrolysis of maltose. No other enzyme can catalyse its hydrolysis.

4. **Optimum temperature and pH** The enzymes are active at moderate temperature (about 37°C) and pH (around 7).

5. **Control of activity of enzymes** The action of enzymes are controlled by various mechanisms and are inhibited by various organic and inorganic molecules.

6. **The activity of most enzymes is closely regulated.**

Coenzymes

In some cases, most active enzymes are associated with some non-protein components required for their activity. These are called prosthetic groups. The prosthetic group which is covalently attached with the enzyme molecule is known as **cofactor**. The prosthetic groups which get attached to the enzyme at the time of reaction are known as **coenzymes**. These are generally metal ions or small organic molecules. The common metal ions are Zn, Mg, Mn, Fe, Cu, Co, Mo, K and Na. Several coenzymes are derived from vitamins such as *thiamine*, *niacin*, *riboflavin*, etc. In some cases, the enzyme activity can be reduced or inhibited by the presence of certain compounds known as **enzyme inhibitors**.

Mechanism : Enzyme Catalysed Reactions

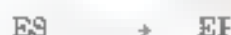
Biochemists are trying to explain the exact molecular basis of enzyme catalysis. The various steps involved in the enzyme catalysed reaction are given below.

(i) Binding of the enzyme (E) to substrate (S) to form a complex.



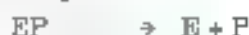
ES is called the enzyme-substrate complex.

(ii) Product formation in the complex



where EP is a complex of enzyme and product.

(iii) Release of product from the enzyme-product complex



These steps are shown in Fig. 8.

The catalytic property of enzymes is present at certain specific regions on their surfaces. These are called active

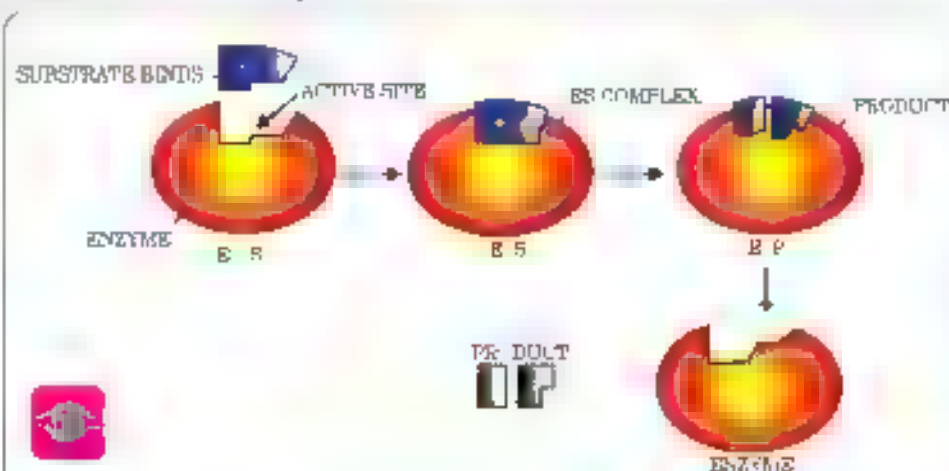


Fig. 8. Enzyme-substrate binding

sites or catalytic sites. The active sites have characteristic shape and fit snugly shaped specific substrate molecules. Specific binding accounts for the high specificity of these enzyme reactions. The specificity of fitting together of the substrate structure and the enzyme structure may be compared as a **key fitting into a lock**. The shape of the active site of any given enzyme is such that only a specific substrate can fit into it, on the same way as one key can open a particular lock.

Applications of Enzymes

1. **Enzyme deficiencies and prevention of diseases** The deficiencies of enzyme in living system cause many diseases. Some of these are given below:

(i) The deficiency of phenylalanine hydroxylase enzyme causes a congenital disease called **phenyl-ketone uria**. This disease causes accumulation of compounds in the body which results into severe brain damage and retardation in children. This can be prevented by a diet with low phenylalanine content.

(ii) Deficiency of enzyme tyrosinase causes **albinism**. Due to deficiency of tyrosinase sufficient melanin, a pigment which gives colour to the skin or hair, is not produced. Therefore, the persons and animals suffering from this disease have white skin or hair.

These diseases can be prevented by the supply of enzymes through diet.

2. **Treating diseases** Certain enzymes are also useful for treating heart diseases. An enzyme **streptokinase** is used to dissolve blood clot to prevent heart attacks.

3. **Industrial applications** The enzymes are widely used in industrial processes. For example, enzymes are used:

- (i) in breweries for the manufacture of beer, wine, etc. by the fermentation of carbohydrates.
- (ii) in food processing industries for preparing sweet, syrup, etc.
- (iii) in the production of cheese by coagulation of milk.

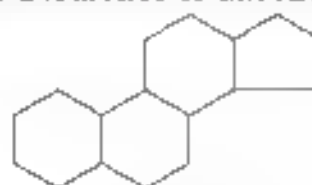
HORMONES

Hormones are the chemical substances which are produced in the ductless glands in the body. These are carried to different parts of the body by the blood stream and control various body functions. Because of the action of hormones as communication among cells, they are called **chemical messengers**. The deficiency of hormones causes metabolic disturbances in the body. In mammals, the secretion of hormones is controlled by the **pituitary gland** of the pituitary gland present at the base of the brain. These hormones are transported to other glands such as **adrenal cortex**, **thyroid** and **sex glands** to stimulate the production of other hormones.

Classification of Hormones

Based upon the structure of hormones, these are classified into three main types:

Steroid hormones These hormones contain a **steroid nucleus** which is based on a four-ring network consisting of three cyclohexane rings and one cyclopentane ring. These are mostly secreted by testes and adrenal cortex of males and are called **sex hormones** or **adrenal cortex hormones**.



Steroid nucleus

The common examples are **testosterone**, **dihydrotestosterone** and **androgens**. During puberty, these stimulate the male sex characteristics. In females, **estrogens** are female sex hormones which are produced in ovaries and are responsible for development of female sex characteristics during puberty.

REMEMBER

Deficiency of enzyme

- phenyl alanine hydroxylase causes disease phenyl ketone uria
- tyrosinase causes disease albinism

Protein or polypeptide hormones. These hormones contain a peptide chain. The common examples are *oxytocin*, *vasopressin* and *insulin*.

a. Amine hormones. These are water soluble compounds which have an amino group and are structurally derived from amino acids. The common examples are *adrenaline* and *thyroxine*.

Examples of Hormones

Some common hormones and their functions are given below.

Table 4: Some typical hormones.

Hormone	Organ of secretion	Functions
STEROID HORMONES		
(a) Sex Hormones		
1. Testosterone	Testes	Regulate the development and normal functioning of male sex organs.
2. Estrogens (Estrone or Estradiol)	Ovary	Control the development and normal functioning of female sex organs.
3. Progesterone	Corpus luteum	Controls the development and maintenance of pregnancy.
(b) Adrenal cortex hormones		
4. Cortisone	Adrenal cortex	Regulate the metabolism of fats, proteins and carbohydrates; control the balance of water and minerals in the body.
PEPTIDE HORMONES		
5. Oxytocin	Posterior pituitary gland	Controls the contraction of the uterus after child birth and releases milk from the mammary glands.
6. Vasopressin	Pituitary glands	Controls the reabsorption of water in the kidney.
7. Insulin	Pancreas	Controls the metabolism of glucose, maintains glucose level in the blood.
AMINE HORMONES		
8. Adrenaline or Epinephrine	Adrenal medulla	Increases pulse rate and controls blood pressure. It releases glucose from liver glycogen and fatty acids from fats in emergency.
9. Thyroxine	Thyroid gland	Controls metabolism of carbohydrates, lipids and proteins.

VITAMINS

These are organic compounds which cannot be produced by the body and must be supplied from outside in order to perform specific biological functions for the normal health, growth and maintenance of body. These are essential to us for the proper functioning of the different organs. They are chemically different from the main nutrients, fats, carbohydrates and proteins. The absence or deficiency of a vitamin can cause specific diseases. Multiple deficiencies caused by lack of more than one vitamins are more common in human beings. This condition of vitamin deficiency is known as **avitaminoses**.

The actual formulae of vitamins are very complicated. For the sake of simplicity these are designated by alphabets, A, B, C, D, E and K. Any subgroup of individual vitamins is designated by the number subscript e.g. A_1 , A_2 , B_1 , B_2 , B_6 , B_{12} , D_2 , D_3 etc., as water soluble or fat soluble.

REMEMBER

- The condition of vitamin deficiency is \Rightarrow **avitaminoses**.
- The condition of excess intake of vitamins is \Rightarrow **hypervitaminoses**.

Classification of vitamins

Vitamins are generally classified into two broad types based on their solubility

Water soluble vitamins

The vitamins which are soluble in water are called **water soluble vitamins**. For example, vitamins B group (B-complex), vitamin C etc. The water soluble vitamins are stored in much lesser amounts in the cells. Water soluble vitamins must be supplied regularly in diet because they are readily excreted in urine and cannot be stored (except vitamin B₁₂) in our body.

Fat soluble vitamins

The vitamins which are soluble in fats are called **fat soluble vitamins**. For example, vitamins A, D, E and K. Liver oils are rich in fat soluble vitamins such as vitamin A and vitamin D. This group of hydrophobic lipid soluble vitamins are not absorbed in the body unless fat digestion and absorption proceed normally. Their deficiency can cause malabsorptive disease. Excess intake of these vitamins may cause **hypervitaminoses**.

It may be noted that vitamin H (Biotin) is neither soluble in water nor in fats.

Sources of Vitamins

Plants can synthesize almost all vitamins whereas only a few vitamins are synthesized in animals. Vitamin D may be supplied through food or may be produced in the skin by irradiation of sterols with sunlight (ultraviolet light). Human body can synthesize vitamin A from carotene and some members of vitamin B-complex and vitamin K are synthesized by micro-organisms present in intestinal tract.

Vitamins are widely distributed in nature both in plants and animals. All cells in the body contain vitamins to some extent. Most of the vitamins have been synthesized and are available commercially. These are generally taken orally.

Functions of Vitamins

The common vitamins, their sources and important functions are given below:

1. Vitamin A (Retinol)

The chemical name of vitamin A is **retinol**. It is a fat soluble vitamin. It is also called **bright eye vitamin**.

- Functions.** (i) It helps in proper growth and normal skeletal development of the body.
(ii) It plays an important role in maintaining proper vision.
(iii) It is also essential for healthy teeth structure.
(iv) It helps in the maintenance of healthy, glowing soft skin.

Sources. Butter, liver, carrots, spinach, ghee, kidney, yellow pumpkin, mustard leaves, whole milk, fish oil, particularly shark liver oil, liver of fresh water fish, tomatoes, coriander leaves, curd, mangoes, egg yolk, cheese, papaya.

Vitamin A is present in the form of carotene in vegetables and fruits which are converted to vitamin A in the body. In general, the darker the colour of the green vegetables, greater is their carotene content.

Deficiency of vitamin A causes *night blindness* and *xerophthalmia* (i.e. hardening of cornea of eye).

Vitamin B - Group

Vitamin B is a water soluble vitamin. It consists of eleven substances. Out of these vitamins, B₁, B₂, B₃ and B₁₂ are important.

2. Vitamin B₁ (Thiamine)

The chemical name of vitamin B₁ is **thiamine**. It is a water soluble vitamin.

- Functions.** (i) Vitamin B₁ helps in carbohydrate metabolism.
(ii) It helps in functioning of heart, nerves and muscles.
(iii) It sharpens our appetite and is sometimes referred to as an "appetite vitamin".

Originally, the term **vitamine** was coined from the word **vital + amine** because the earliest identified compounds had amino groups. Later studies showed that most of them did not contain amino groups, so the letter 'e' was dropped and the term **vitamin** is used these days.

Sources. Milk, pulses, wheat, bran, sea food, yeast, whole grain cereals, green vegetables, soyabean, dairy products (except butter).

The deficiency of vitamin B₁ causes *beri-beri*.

3. Vitamin B₂ (Riboflavin)

The chemical name of vitamin B₂ is **riboflavin**. It is a water soluble vitamin.

Functions. (i) It helps in oxidation and utilisation of oxygen.

(ii) It helps in carbohydrate and protein metabolism.

(iii) It is necessary to keep the skin healthy.

(iv) It helps in the normal functioning of the eye.

Sources. Meat, whole grains and pulses, milk, yeast, liver, peas, eggs, green vegetables.

The richest sources of riboflavin is dried yeast and liver.

The deficiency of vitamin B₂ causes cracking of skin, lips, corners of the mouth, photophobia (rough eye lids), dark red tongue, glossitis.

4. Vitamin B₃ (Niacin)

Vitamin B₃ is also called **niacin**. It is a water soluble vitamin belonging to the B-complex group. It is one of the most stable of vitamins.

Functions. It is needed for the metabolism of carbohydrates, fats and proteins.

(i) It keeps the skin healthy.

(ii) It gives sound mental health.

(iii) It has most important positive contribution to good nutrition.

Sources. Milk, fish, legumes, potatoes, green leafy vegetables, meat, eggs, fowl (chicken), whole grain.

The deficiency of vitamin B₃ causes pellagra.

5. Vitamin B₆ (Pyridoxine)

It is called **pyridoxine**. It is a water soluble vitamin. In fact, it is a mixture of three substances, *pyridoxine*, *pyridoxal* and *pyridoxamine*.

Sources. Cereals, grains, moussee, yeast, meat, fish, egg yolk, rice bran.

The deficiency of vitamin B₆ causes severe dermatitis, convulsions, anaemia, etc.

6. Vitamin B₁₂ (Cyanocobalamin)

The chemical name of vitamin B₁₂ is **cyanocobalamin**. It is also a water soluble vitamin.

Functions. (i) It is essential for the metabolism of nervous tissue.

(ii) It is necessary for the formation of healthy blood and proper growth of the body.

(iii) It is essential for preventing the disease called pernicious anaemia.

Sources. Liver, cheese, milk, eggs, kidney, fish, meat.

The deficiency of vitamin B₁₂ causes *pernicious anaemia*, inflammation of tongue and mouth.

7. Vitamin H (Biotin)

It is also called **biotin**.

It is neither soluble in water nor in fat.

Sources. Yeast, liver, kidney and milk.

The deficiency of vitamin H causes dermatitis, depression, loss of hair and paralysis.

8. Vitamin C (Ascorbic acid)

The chemical name of vitamin C is **ascorbic acid**. It is the most highly soluble in water.

Functions. It is necessary for keeping teeth, gums and joints healthy.

(i) It plays an important role in normal metabolism of the amino acids.

is, It helps in healing of cuts and wounds.

(iv) It gives resistance to our body against diseases and infections.

Sources. Amla, tomatoes, mangoes, oranges, pears, pineapple, cabbage, apples, lemon, lime, green chilies, guava.

Amla is a good source of vitamin C.

The deficiency of vitamin C causes scurvy.

9. Vitamin D (Ergocalciferol,

It is also called calciferol.

It is a fat soluble vitamin. It is formed in the skin under the action of sunshine.

Functions. (i) It keeps the bones and teeth healthy.

(ii) It helps in the utilisation of calcium and phosphorus.

Sources. Cod liver oil, butter, milk, egg yolk, fish, ghee, cheese.

Exposure to sunlight provides another method of production of vitamin D in the body itself.

The deficiency of vitamin D causes rickets.

10. Vitamin E (Tocopherol)

The chemical name of vitamin E is tocopherol. *It is a fat soluble vitamin.*

Functions. It plays an important role in the protection of vitamin A, carotene and ascorbic acid.

It is necessary for the normal reproduction and protection of the liver.

Sources. Vegetable oils, milk, tomatoes, dark green leafy vegetables, eggs, kidney, whole grain cereals, nuts, liver.

The deficiency of vitamin E causes loss of sexual power of reproduction.

11. Vitamin K (Phylloquinone)

It is also known as phylloquinone.

It is a fat soluble vitamin. It is also called coagulation vitamin.

Functions. It helps in clotting of blood and prevents haemorrhage.

Some important vitamins, their sources and the diseases caused by deficiency of these are listed below.

Vitamin	Chemical Name	Deficiency Disease	Sources of Vitamin
A	Retinol Bright eye vitamin	Xerophthalmia or hardening of corners of eye or night blindness	Cod liver oil, shark liver oil, carrot, ripe papaya, liver, kidney, butter, milk etc.
B ₁	Thiamine	Beriberi, loss of appetite, retarded growth, diseases of nervous system	Milk, rice, yeast, nuts, eggs, green vegetables, liver, kidney
B ₂	Riboflavin	Glossitis, dark red tongue, dermatitis and cheilosis (fissuring at corners of mouth and lips).	Turnip, milk, eggs, yeast, vegetables, liver, kidney
B ₆	Pyridoxine	Dermatitis and convulsions.	Yeast, milk, meat, fish, egg yolk, whole cereal, grains.
B ₁₂	Cyanocobalamin	Pernicious anaemia, RBC deficiency, in haemoglobin, inflammation of tongue and mouth.	Meat, eggs, liver of ox, sheep, pig, fish, curd, etc.
C	Ascorbic acid	Scurvy, bleeding of gums, pyorrhoea, loosening and bleeding of teeth.	Citrus fruits like orange, lemon, amla, guava, green vegetables.
D	Ergocalciferol	Rickets, bone deformities in children and osteomalacia, soft bones and joint pains in adults.	Milk, egg yolk, cod liver oil, exposure to sunlight.
E	Tocopherol	Sterility	Oil like cotton seed oil, soyabean oil, wheat, grain oil, sunflower oil.
K	Phylloquinone	Haemophilia, haemorrhagic condition, increased blood clotting time.	Cereals, green leafy vegetables.
H	Biotin	Dermatitis, loss of hair and paralysis.	Yeast, liver, kidney and milk.
Q ₁₀	Coenzyme	Low order of immunity of body against many diseases.	Chloroplasts of green plants and mitochondria of animals.

Sources. Green leafy vegetables, soyabean, cabbage, vegetable oil, spinach, tomatoes.

The deficiency of vitamin K causes haemorrhage, lengthens the time of blood clotting.

13. Coenzyme Q_{10}

Sources. The main sources of coenzyme Q_{10} are chloroplasts of green plants and mitochondria of animal.

The deficiency of coenzyme Q_{10} causes low order of immunity of body against many diseases.

Differences between Hormones and Vitamins

Both hormones and vitamins are required in small amounts to bring out various metabolic and physiological reactions in the body. These have some differences as given below.

Hormones	Vitamins
1. These are chemical substances which are produced in the ductless glands in the body.	These are not produced in the body (except vitamin D) but have to be supplied in diet and are essential for proper functioning of the different organisms.
2. These are not stored in the body but are continuously produced.	These may be stored in the body to fight out diseases.

NUCLEIC ACIDS

As you know, every generation of each and every species resembles its ancestors in many ways. It has been established that the nucleus of a living cell is responsible for transmission of these characteristics (also called heredity) from one generation to the next. The particles present in the nucleus of the cell which are responsible for transmission of inherited characters are called **chromosomes** which are made up of proteins combined with biomolecules known as nucleic acids. *Nucleic acids are biologically important polymers which are present in all living cells.*

They play an important role in the development and reproduction of all forms of life. They direct the synthesis of proteins and are responsible for the transfer of genetic information, i.e., the hereditary characteristics. The repeating units of nucleic acids are called *nucleotides*. Therefore, the nucleic acids are also regarded as **polynucleotides**. While proteins have a polypeptide chain, nucleic acids contain a polypeptide ester chain.

There are two types of nucleic acids:

- DNA (deoxyribonucleic acid)
- RNA (ribonucleic acid).

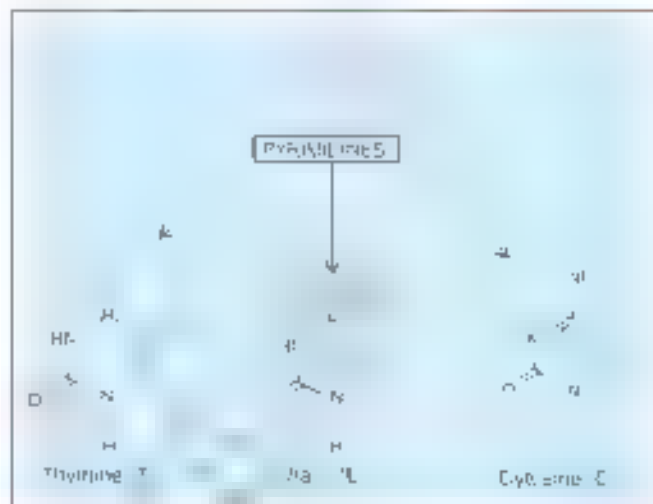
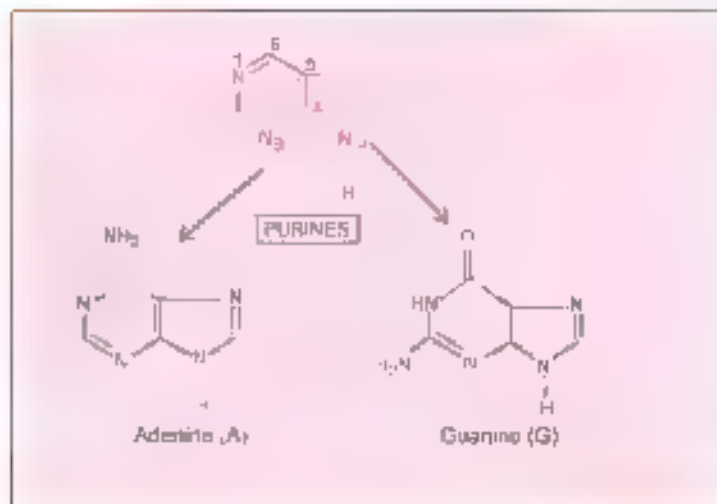
A nucleotide consists of three chemical components:

- A nitrogen containing heterocyclic base
- a five carbon sugar
- a phosphate group.

1. Nitrogen containing heterocyclic base. There are two different types of heterocyclic nitrogenous bases. These are known as **purines** and **pyrimidines**. Pyrimidines have a single heterocyclic ring while purines have two fused rings. The heterocycles present in nucleic acid are substituted forms of these compounds. The common examples are:

- adenine (A) and guanine (G) are substituted purines
- cytosine (C), thymine (T) and uracil (U) are substituted pyrimidines.

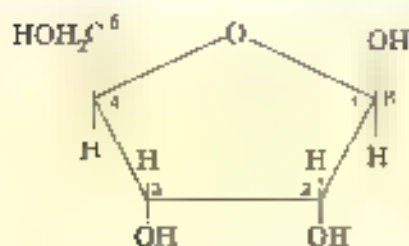
The structures of these compounds are shown below



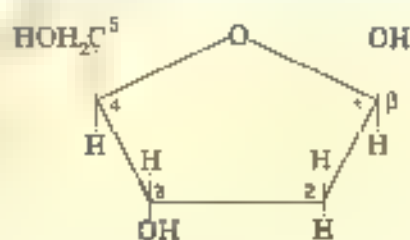
are found in both polymers DNA and RNA.

RNA contains **uracil** instead of **thymine** present in DNA.

2. Sugars: There are two types of sugars present in nucleic acids. The sugar present in RNA is β -D-ribose and in DNA is β -D-2-deoxyribose as shown below



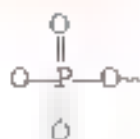
β -D-Ribose (a sugar present in RNA).



β -D-2-Deoxyribose (a sugar present in DNA)

3. Phosphate group: These are responsible for the linkage in nucleic acid polymers.

The phosphate group in nucleic acid is



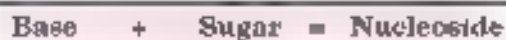
Phosphate unit

The phosphate group is bonded to a hydroxyl group of sugar

Nucleosides and Nucleotides

Nucleosides

The molecules in which one of the nitrogen bases (purine or pyrimidine) is bonded with a sugar molecule is called **nucleoside**.



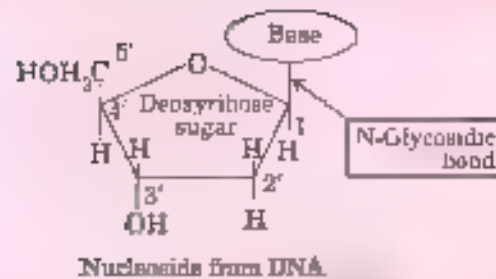
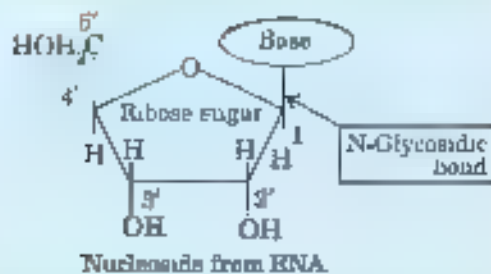
The nucleosides of RNA and DNA differ in two respects

1. The sugar in RNA nucleoside is **ribose** while the sugar in DNA nucleoside is **deoxyribose**.

2. The nucleoside of RNA contains uracil base in place of thymine present in DNA.

REMEMBER

The suffix **-2-deoxy** in the name of 2-deoxyribose means the **absence** of oxygen at position-2.



It may be noted that in nucleosides, the carbon atoms of sugar molecule are numbered as 1' 2' 3' 4' 5' in an order to distinguish these from the bases. The purine or pyrimidine bases are attached to position 1' of pentoses through **N-glycosidic linkages**.

The nucleosides are named depending upon the base present as

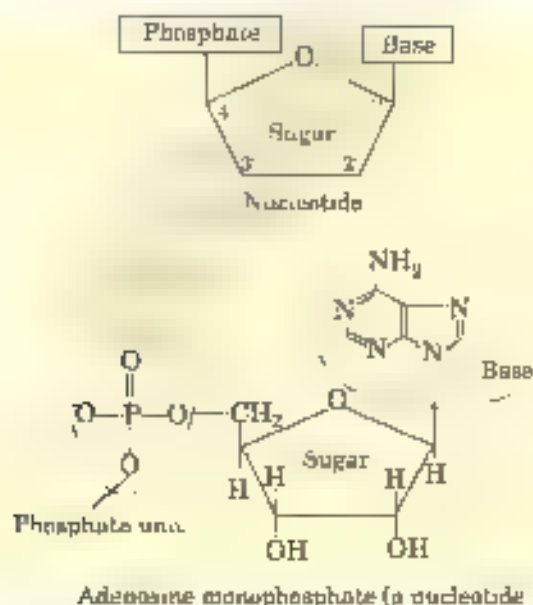
Base	Abbreviation	Nucleoside
Adenine	A	Adenosine
Guanine	G	Guanosine
Cytosine	C	Cytidine
Thymine	T	Thymidine
Uracil	U	Uridine

Nucleotides

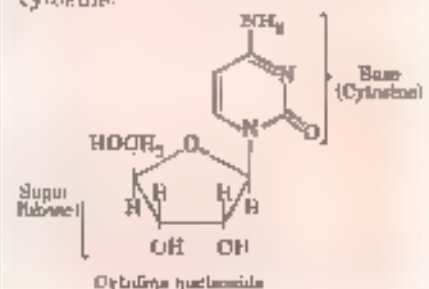
When the phosphate group is attached to the nucleoside, the compound formed is called **nucleotide**. In other words, a nucleotide is a phosphate ester of nucleoside as it consists of a purine or pyrimidine base, the 5-carbon sugar and one or more phosphate groups.



Thus, a nucleotide contains a sugar unit linked to nitrogen base and phosphate group unit. Their structures are shown below:



The nucleoside **cytidine** is formed from sugar ribose and the base cytosine.



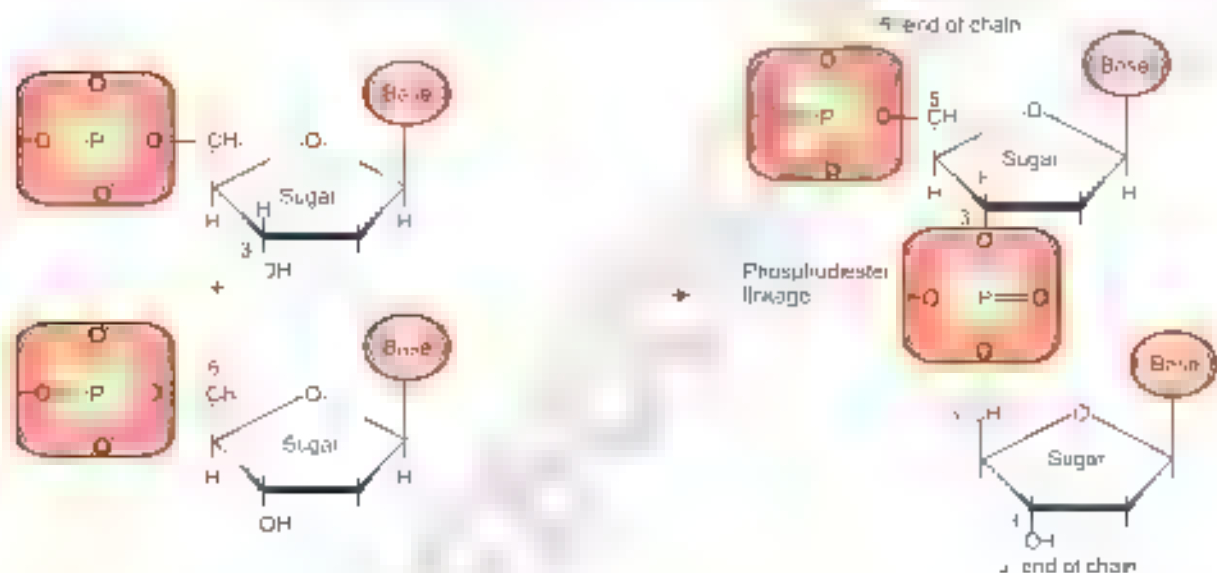
In nucleosides, the sugar rings are attached to the nitrogen atom of the heterocyclic ring by a bond between 1' atom of sugar and nitrogen atom of

heterocyclic ring. This linkage is called **glycosidic bond**. The phosphate group is bonded to a hydroxyl group of sugar.

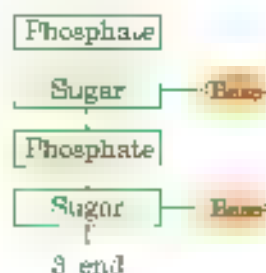
The nucleotides are abbreviated by three capital letters preceded by *d-* or *r-* in case of deoxy series. For example

- AMP Adenosine monophosphate
- DMP Deoxyadenosine monophosphate
- ATP Adenosine triphosphate
- UDP Uridine diphosphate

Nucleotides are joined together by **phosphodiester linkages** between 5' and 3' carbon atoms of pentose sugar. The formation of a dinucleotide is shown below.

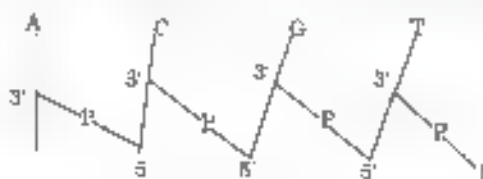


This may be simplified represented as

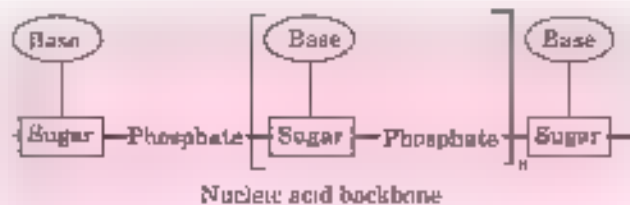


Therefore, the consecutive joining of sugar unit of one nucleotide to the phosphate group of next nucleotide results in a long chain polymer called **nucleic acid**. A nucleic acid chain is commonly abbreviated by a one letter code with the 5' end of the chain written on the left side. For example, a tetranucleotide having adenine, cytosine, guanine and thymine bases from 5' end to 3' end is written as ACGT.

The backbone of the nucleic acid consists of a repeating sugar and phosphate bonds. For simplicity, the bases are represented by their respective symbols, the phosphate unit is represented by the symbol 'P' and sugar is drawn using its simple Fischer projection. For example, the tetranucleotide ACGT can be written as

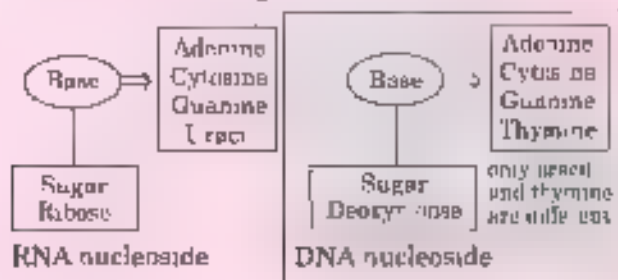


Thus, the nucleic acid backbone consists of a ternary sugar-phosphate residues. One of the four nitrogen base residues is attached to each sugar unit on this backbone. The nucleic acid backbone is shown below.



Summary of Nucleic Acids

Base and sugars form **Nucleosides**



⇒ **RNA contains uracil, while DNA contains thymine, other bases are same.**
Nucleosides joined to phosphate group form **nucleotides**. The polymers of nucleotides are **nucleic acids**.

STRUCTURE OF DNA

1. Primary Structure of DNA

The sequence of nucleotides in the chain of nucleic acid is called its **primary structure**. It was found by **E. Chargaff** that the base composition of DNA varied from one species to other species. However, in any species, the amount of adenine was equal to that of thymine ($A = T$) and the amounts of cytosine was equal to that of guanine ($C = G$). This is also known as **Chargaff rule**. In other words, the total amount of purines was equal to that of pyrimidines ($A + G = C + T$). But the ratio $A/T/C/G$ varied considerably between species. For example the $A/T/C/G$ ratio is 1.52 in man and about 0.98 in *E. Coli*.

The three dimensional structure of DNA was elucidated by **James Watson** and **Francis Crick** in 1953 on the basis of X-ray diffraction studies. Watson and Crick proposed that DNA polymers have **double helical structure**, which explained not only the base equivalence ($A = T$ and $C = G$) but other properties of DNA especially its duplication in a living cell called **replication**. The double helical structure of DNA is shown in Fig. 7.

This double helical structure of DNA consists of two right handed helical polynucleotide chains coiled around the same central axis. The two strands are antiparallel i.e. their 5' → 3' phosphodiester linkages run in opposite directions. These two strands are marked 5' and 3' which indicate that the free hydroxyl groups of the terminal deoxyribose units are present at 5' and 3' positions respectively. Therefore a linear polymer has a free 5-hydroxyl group at one end and a free 3-hydroxyl group at other end. The nucleotides making up each strand of DNA are connected by phosphate ester bonds. This forms the **backbone** of each DNA strand from which the bases extend (Fig. 7). The bases (purines and pyrimidines) are stacked inside the helix in planes perpendicular to the helical axis. It is like a stack of flat plates held together by two ropes of sugar-phosphate polymeric backbone running along outside of stack. The bases project towards each other within this structure, while the sugar and phosphate components form a structural framework on the outside of the duplex. The bases, thus are the steps of the spiral staircase and the sugar phosphate framework is

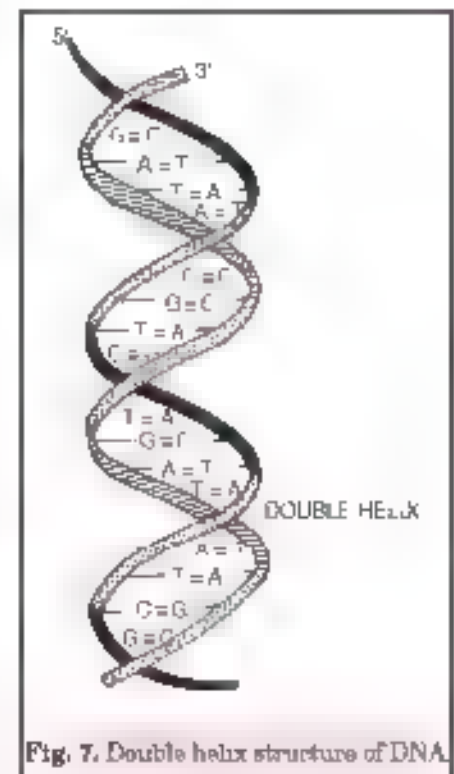
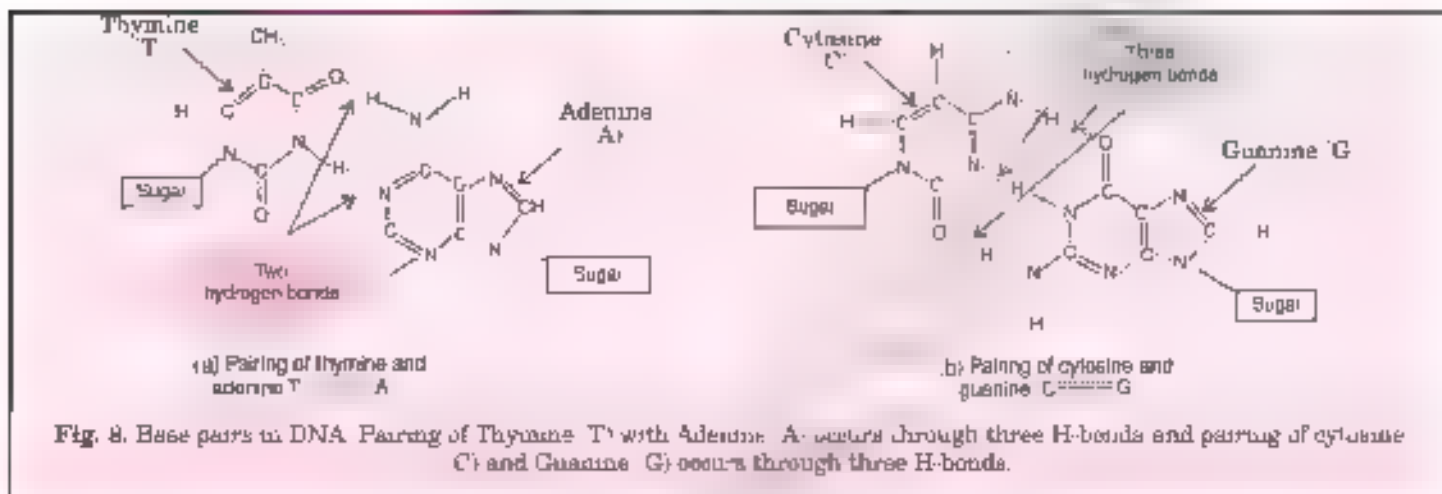


Fig. 7. Double helix structure of DNA.

the coding. Such a structure is called **double helix structure**. The order in which bases occur is called the **base sequence**. As a convention, the bases are abbreviated by the first letters.

2. Secondary structure of DNA

The two strands are held together by hydrogen bonds. This hydrogen bonding is very specific because the structures of bases permit only one mode of pairing. For example, guanine is hydrogen bonded to cytosine and adenine to thymine. **Thymine and adenine can be joined by two hydrogen bonds while cytosine and guanine can be joined by three hydrogen bonds.** This has been shown in Fig. 8. No other combination of four bases is possible because these do not lead to strong hydrogen bonds.



The two strands may be represented as

Strand I	A	T	T	A	A	C
Strand II	T	C	A	G	T	C

REMEMBER

- Adenine and Thymine form two hydrogen bonds with an overall strength of about 42 kJ mol^{-1} .
- Guanine and Cytosine form three hydrogen bonds with overall strength of about 71 kJ mol^{-1} .

It may be remembered that only A and T and G and C can combine. A and T are joined by two hydrogen bonds while G and C are joined by three hydrogen bonds. In addition to hydrogen bonds, other forces such as hydrophobic interactions between stacked bases are also responsible for stability and maintenance of double helix.

The two strands of DNA are said to be **complementary** to each other in the sense that the sequences of bases in one strand automatically determines that of other. For example, whenever adenine (A) appears in one strand a thymine (T) appears opposite to it in the other strand.

The diameter of double helix is 2 nm and the double helical structure repeats at interval of 3.4 nm when it completes one turn. Thus one turn corresponds to ten base pairs. DNA helices can be right handed as well as left handed. The β -conformation of DNA having right handed helices is most stable. On heating the two strands of DNA separate from each other and this process is known as **melting**. When these two strands are cooled they again hybridize. This process is called **annealing**. The temperature at which the two strands completely separate is known as its melting temperature (T_m). This is specific for each specific sequence.

SOLVED EXAMPLES

Example 3.

In E. coli DNA, the AT/GC ratio is 1.08. If the number of moles of adenine in this DNA sample are 465,000, calculate the number of moles of guanine present.

Solution : We know that the number of moles of adenine should be equal to those of thymine. Therefore

$$A + T = 2 \times 465,000 = 930,000$$

Now $A + T/G + C = 1.09$

$$G + C = \frac{A + T}{0.99} = \frac{930,000}{0.99} = 1,000,000$$

Now moles of guanine should be equal to cytosine

$$G = \frac{1,000,000}{2} = 500,000.$$

□ Example 4

A DNA molecule with more number of GC base pairs than AT base pairs has higher T_m than the one with lesser number of GC base pairs than AT base pairs. Explain why?

Solution : DNA molecule with more number of GC base pairs than AT base pairs has higher T_m because GC base pairs having 3 hydrogen bonds compared to AT base pairs having only 2 hydrogen bonds results in stronger bonding. Therefore T_m is high.

□ Example 5

Two samples of DNA, X and Y have melting temperature T_m as 340 and 350 K respectively. What do the data indicate regarding their base composition?

N.C.E.R.T.

Solution : We know that GC are held by triple hydrogen bonds while AT are held by two hydrogen bonds. Therefore GC base pair results into stronger bonding. Thus, the sample Y having higher T_m must be having more GC content as compared to sample X.

Structure of RNA

The structure of RNA is similar to that of DNA except that it is a **single strand structure**. Sometimes, they fold back on themselves to form a double helix structure. RNA molecules are of three types and they perform different functions. They are named as

- i) messenger RNA : *m-RNA*
- ii) ribosomal RNA : *r-RNA*
- iii) transfer RNA : *t-RNA*

BIOLOGICAL FUNCTIONS OF NUCLEIC ACIDS

DNA is the chemical basis of heredity and may be regarded as the reserve of genetic information. DNA is exclusively responsible for **maintaining** the identity of different species of organisms over an **infinite** of years. The important biological functions of nucleic acids are

1. Replication

It is the property of a molecule to synthesise another molecule. DNA has a unique property to **duplicate or replicate itself**, i.e. it can bring about the synthesis of another DNA molecule. Replication of DNA is an enzyme catalysed process. In this process, at the time of cell division (mitosis) the two strands of DNA double helix partly unwind and each strand serves as a template or pattern for the synthesis of a new DNA molecule (strand). Due to unique specificity of base pairing, the newly synthesised complementary strand in each case is an exact copy of the originally separated strand. As a result, two double stranded DNA molecules are formed called two daughter DNA molecules. One of the strand comes from the parent DNA molecule and the other is newly synthesised. Each DNA is exact replica of the parent. In this way, hereditary effects are transmitted from one cell to another. This is shown in Fig. 9.

It may be noted that DNA replication follows the base pairing rules by which A pairs with T and G pairs with C. This replication can easily be understood. Suppose a segment along a double helix is

A	G	C	A	A	T
T	C	G	T	T	A

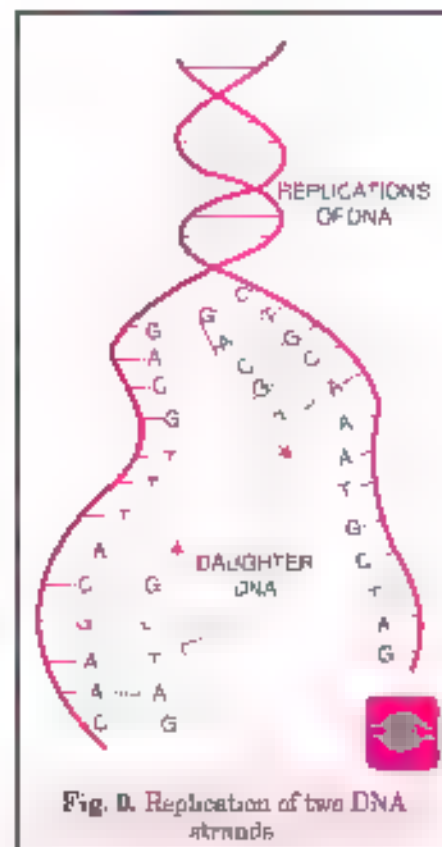
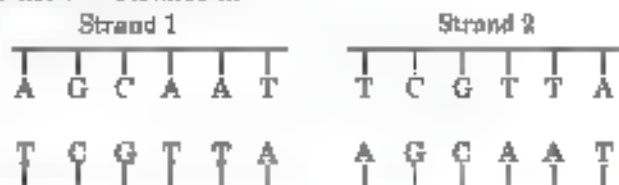


Fig. 9. Replication of two DNA strands

When this double helix unravels, then it forms two strands as



Each strand can act as a template to build identical double helices. The complements to the two strands are



These two double helices are identical to each other and to the first double helix. Thus, the original double helix is repeated itself.

The DNA replication is **semi-conservative** i.e. only half of the parental DNA is conserved and only one strand is synthesized. DNA replication takes place only in the 5' → 3' direction.

4. Protein Synthesis

DNA molecules also perform an important function of synthesising proteins, which serve as machinery of the living cell. In this process, the genetic information coded in DNA in the form of specific base sequences is translated and expressed in the form of sequence of amino acids which result in the synthesis of specific proteins which perform various functions in the cell. Actually, the proteins are synthesised by various RNA molecules in the cell but the message for the synthesis of a particular protein is coded in DNA.

Protein synthesis is a fast process and about 20 amino acids are added in one second. For example, silk has the major component fibroin protein. A single fibroin gene makes 10^4 copies of its mRNA and each mRNA produces 10^2 molecules of fibroin protein amounting to a total of 10^6 molecules of protein per cell in a period of 4 days.

Differences between DNA and RNA

The important differences between DNA and RNA are

DNA	RNA
It occurs mainly in the nucleus of the cell.	It occurs in the cytoplasm of the cell.
It has double stranded α -helix structure in which two strands are coiled spirally in opposite directions.	It has single stranded α -helix structure.
The sugar molecule is 2-deoxyribose.	The sugar molecule is ribose.
Nitrogenous base uracil is not present.	Nitrogenous base thymine is not present.
DNA has the unique property of replication.	RNA usually does not replicate.
It is responsible for the transmission for hereditary character.	Helps in protein biosynthesis.
DNA molecules are very large, their molecular masses may vary from 6×10^6 to 10^8 .	RNA molecules are much smaller with molecular mass ranging from 2×10^4 to 4×10^4 .

Competition Plus

- Q LIPIDS are oily, fatty or waxy substances present in living organisms. They form part of structure of biological membranes and store energy for the cell.
- Q CELLULAR MEMBRANES are constituted mainly of phospholipids and cholesterol. For details refer Competition File (page 68).

Learning Plus

DNA Fingerprinting

Every individual has unique fingerprints. These occur on the tips of the fingers and have been used for identification for a long time. However, these may be changed by surgery. The unique fingerprints are due to unique sequences of bases on DNA for every person. The difference between people or animals is the difference in the order of the base pairs. There are so many millions of base pairs in each person's DNA that every person has a different sequence. This technique for identifying an individual person, organism based upon the uniqueness of their DNA pattern is called **DNA fingerprinting**. It is same for every cell and cannot be altered by any known treatment. It may be noted that the patterns do not give an individual fingerprints but they are able to determine whether two DNA samples are for the same person, related person or non-related person.

The important uses of DNA fingerprinting are

- (i) in forensic laboratories for identification of innocence or guilt in criminal cases
- (ii) to determine paternity of an individual
- (iii) to identify dead bodies in any accident by comparing the DNA prints of parents or children
- (iv) to identify racial groups to rewrite biological evolution

Learning Plus

Gene. Each segment of a DNA molecule that codes for a specific protein or a polypeptide is called **gene**.

Genetic code. The relation between the nucleotide triplet and the amino acids is called the **genetic code**.

Mutation. It is a chemical change in the sequence of nitrogenous bases in DNA molecule that could lead to synthesis of proteins with different amino acid sequence. The changes in DNA molecule can occur spontaneously or it may be caused by radiation, chemical agents or viruses. Most of these changes in the DNA molecule are normally being repaired by special enzymes in the cell. The altered proteins caused by mutation may lose their biological activities and thus causing the death of the cell. The defective genes can also cause abnormalities or diseases.

SOLVED EXAMPLES

Example 8.

What will be the sequence of bases on the strand of DNA that would be complementary to strand having the following sequence of bases:

A A T C G T A G G C

Solution: We know that adenine (A) pairs only with thymine (T) and cytosine (C) pairs only with guanine (G), we can write the sequence of bases as

Original strand	A A T C G T A G G C
Complementary strand	T T A G C A T C C G

add on

Conceptual Questions 2

Q.1 (i) Which vitamin deficiency causes rickets?

(Karnataka S.B. 2018)

(ii) Name the base that is found in nucleotide of RNA only.

(CBSE Sample Paper 2017-18)

Ans. (i) Vitamin D

(ii) Uracil

Q.2. How many naturally occurring amino acids in proteins exist? How many of these are synthesised by the body?

Ans. There are 20 amino acids in proteins. 10 out of these can be synthesised by human body.

Q.3. What is the difference between DNA and RNA on the basis of bases they contain?

Ans. Both DNA and RNA contain two bases derived from purine, guanine and adenine and one base derived from pyrimidine cytosine. However, they have fourth different base. DNA contains thymine whereas RNA contains uracil.

Q.4. State differences between primary and secondary structure of proteins.

Ans. The order in which the amino acids are joined to one or more polypeptide chains of a protein is called primary structure. It gives its function and is critical of its biological activity.

The secondary structure determines the manner in which the protein chain is folded. It arises from the planar geometry of the peptide bond and hydrogen bonds between one region of the backbone to another.

Q.5. Which α -amino acid can cross link peptide chains?

Ans. Cysteine can cross link peptide chains through disulphide bonds.

Q.6. State the use of interferon and insulin in medicines.

Ans. Interferon is an antiviral agent. Insulin is used in treatment of diabetes.

Q.7. What type of linkages hold together monomers of DNA?

(Assam S.B. 2018)

Ans. Hydrogen bonds

Q.8. What are the main functions of the hormone adrenaline ?

Ans. The main functions of adrenaline are

It increases the pulse rate and blood pressure.

(ii) It releases glucose from glycogen and fatty acids from fats.

Q.9. Which enzyme is present in saliva ? What is its function ?

(H.P.S.B. 2012)

Ans. The enzyme present in saliva is amylase. It hydrolyses starch into maltose.

Q.10. Which of the following is not an α -amino acid ?

Cysteine, Tyrosine, Tryptan, Proline, Serine

Ans. Tryptan

Q.11. What are non-essential amino acids? Give one example.

(Assam S.B. 2017, H.P.S.B. 2018)

Ans. The amino acids which can be made by our bodies and are not required in diet are called non-essential amino acids. For example, glycine.

Q.12. How are nucleosides, nucleotides and nucleic acids related ?

Ans. Nucleosides joined to phosphate group form nucleotides. The polymers of nucleotides are nucleic acids.

Q.13. What is prosthetic group ?

Ans. A prosthetic group is a non-protein portion obtained by hydrolysis of conjugated proteins. The main function of the prosthetic group is to control the biological functions of proteins.

Q.14. What is the function of enzyme present in liver ?

Ans. The enzyme present in liver converts galactose to glucose.

Q.15. Fresh tomatoes are a better source of vitamin C than those present in tomatoes which have been stored for some time.

(Manipal S.B. 2017)

Ans. On prolonged exposure to air, vitamin 'C' present in stored tomatoes is destroyed due to its aerial oxidation.

Q.16. Name the enzyme which converts sucrose into glucose and fructose.

(Pb.S.B. 2005, 2012)

Ans. Invertase

Q.17. Name the enzyme which converts

(i) maltose into glucose (ii) glucose into alcohol.

(Pb.S.B. 2012)

Ans. (i) Maltase

(ii) Zymase.

Q.18. What is hypervitaminoses and avitaminoses ?

(Pb.S.B. 2012)

Ans. Excess intake of vitamins A and D causes hypervitaminoses. Multiple deficiencies caused by lack of more than one vitamins is called avitaminoses.

Q.19. What is coenzyme ? Give one example.

Ans. The non-protein component of an enzyme which is loosely held by the enzyme and is essential for its biological activity is called a coenzyme. These are mostly derived from vitamins such as thiamine (B₁), riboflavin (B₂) etc.

Q.20. What is isoelectric point ?

(Pb. S.B. 2003)

Ans. The pH at which no net migration of amino acid takes place under the influence of an applied electric field is called isoelectric point. For example, isoelectric point of glycine is 5.1.

Q.21. Name the vitamins in each case whose deficiency causes

(i) night blindness (ii), poor coagulation of the blood.

(C.B.S.E. Sample Paper 2010)

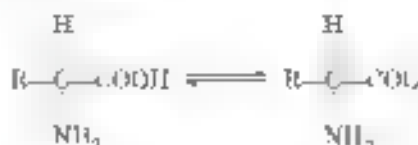
Ans. (i) Vitamin A

(ii) Vitamin K

Q.22. Amino acids have high melting points and are soluble in water.

(C.B.S.E. Sample Paper 2010)

Ans. Amino acids have high melting points and are soluble in water because these exist as zwitter ions or dipolar ions as



Because of dipolar ions, there are strong intermolecular forces in crystals and they behave as ionic compounds.

Q.23. What is meant by the secondary structure of proteins ?

(C.B.S.E. Sample Paper 2016)

Ans. The secondary structure gives the manner in which polypeptide chains are folded or bent. This arises from the plane geometry of the peptide bond and hydrogen bond between one region of the backbone to another.

Pauling and Corey investigated the structures of many proteins with the help of X-ray patterns. It was observed that in many proteins, polypeptide chains are coiled up in the form of a spiral staircase called helix or α -helix. The helical shape results from the formation of hydrogen bonds between amino acids in the peptide chain. This structure can be imagined as if one can coil a polypeptide chain around an invisible cylinder.

In addition, the another type of secondary structures are also known such as β -pleated sheet and triple helix.

Q.24. Give one example each for essential and non-essential amino acids.

(CBSE Sample Paper 2011)

Ans. Essential amino acid : Valine

Non-essential amino acid : glycine

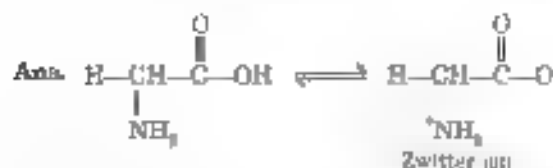
Q.25. Differentiate between keratin and insulin.

(BSE Sample Paper 2011)

Ans. Keratin is a fibrous protein while insulin is a globular protein.

Q.26. Write the Zwitter ion structure of glycine.

(CBSE Sample Paper 2011, Karnataka S.B. 2018)



Q.27. What type of forces are responsible for the formation of β -pleated sheet structure ? (H.P.S.B. 2012)

Ans. Hydrogen bonds

Q.28. Write the chemical name of vitamin B₁₂.

(Mizoram S.B. 2012)

Ans. cyanocobalamin.

Q.29. What is the chemical name of vitamin C and which disease is caused by its deficiency?

(Pb. S.B. 2013, H.P.S.B. 2017)

Ans. Ascorbic acid, deficiency disease : Scurvy

Q.30. What is the chemical name of vitamin A and which disease is caused by its deficiency? (Pb. S.B. 2013)

Ans. Retinol, deficiency disease : Xerophthalmia

Q.31. What are three types of RNA molecules which perform different functions?

Ans. Messenger RNA (m-RNA), ribosomal RNA (r-RNA) and transfer RNA (t-RNA).

Q.32. Vitamin C is found in fruits and vegetables. It cannot be stored in our body. Why?

(Kerala S.B. 2014, Meghalaya S.B. 2017)

Ans. It is soluble in water and excess of it is readily excreted in urine.

Q.33. Name the vitamins whose deficiency cause (i) rickets (ii) night blindness, (iii) scurvy.

(Manipur S.B. 2011)

Ans. (i) Vitamin D (ii) Vitamin A (iii) Vitamin C

Q.34. Which amino acid is not optically active ?

(Meghalaya S.B. 2018)

Ans. Glycine : $\text{NH}_2\text{CH}_2\text{COOH}$

Q.35. Name the metal present in vitamin B₁₂.

(H.P.S.B. 2013)

Ans. Cobalt

Q.36. Name the nitrogenous base present in RNA but not in DNA.

(Karnataka S.B. 2018)

Ans. Uracil

Q.37. Name one fibrous protein and one globular protein.

(Meghalaya S.B. 2018)

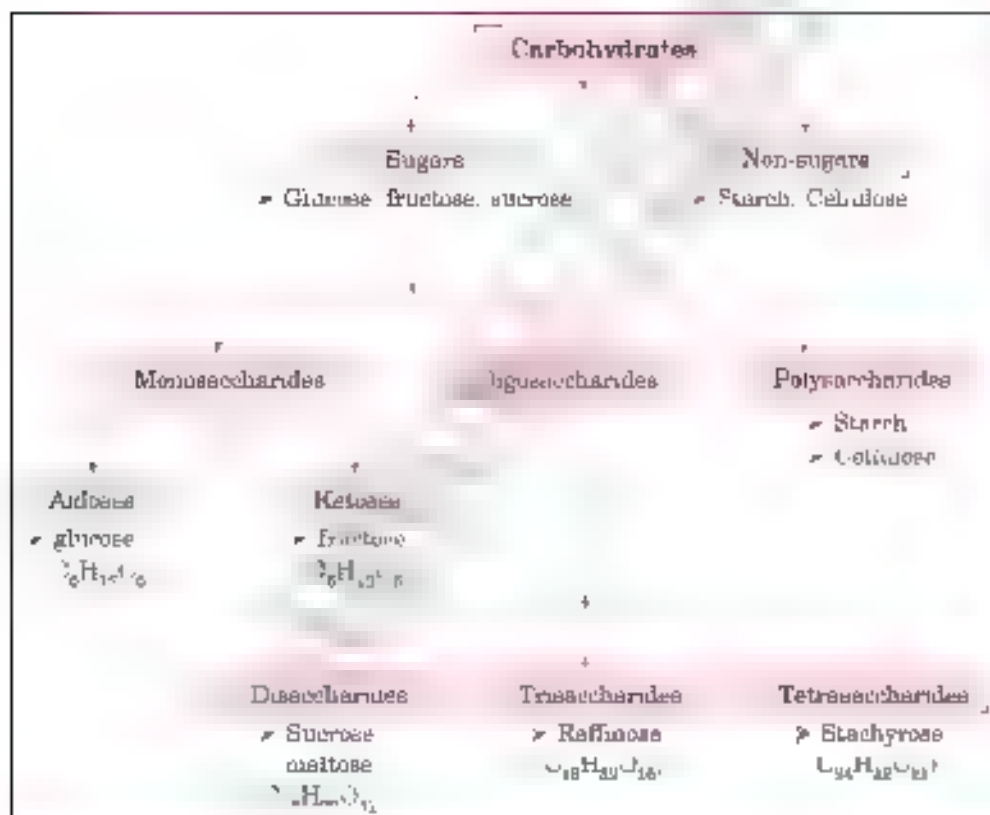
Ans. Fibrous : Keratin

Globular : Albumin

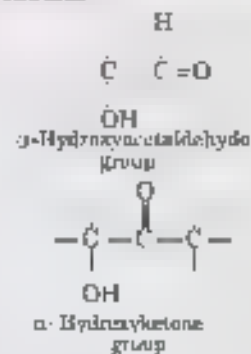
Key Terms & Laws

- **Carbohydrates** are polyhydroxy aldehydes or ketones having the general formula, $C_x(H_2O)_y$ and are ultimate source of our food
- **Anomers** The pair of optical isomers which differ in the configuration only around C atoms e.g. α -D-glucose and β -D-glucose
- **Mutarotation** The spontaneous change in specific rotation of an optically active compound with time to an equilibrium value
- **Invert sugar** The change of sign of rotation on hydrolysis of sucrose is called **inversion reaction** and the mixture of glucose and fructose is called invert sugar
- **Amino acids** are organic compounds containing both amino group $-NH_2$ and carboxylic acid group $-COOH$.
- **Proteins** are complex long polymers of amino acids linked by $-CO-NH$ bonds
- **Enzymes** are biological catalysts produced by living cells which catalyse the biochemical reactions.
- **Vitamins** are essential components of our diet
- **Nucleic acids** are biomolecules which are found in the nuclei of all living cells in the form of nucleoproteins
- **Mutation** The chemical change in a DNA molecule that would lead to synthesis of proteins with different amino acid sequence
- **Replication** The process in which duplication of DNA takes place during cell division

QUICK CHAPTER ROUND UP



- **Reducing sugar** which reduces Fehling solution or Tollen's reagent. They contain



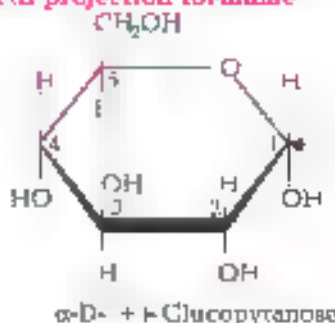
or

e.g. D-glucose, D-fructose, maltose, lactose

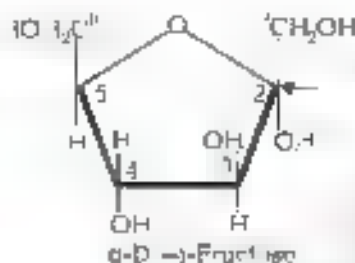
- **Non-reducing sugars** which do not reduce Fehling solution or Tollen's reagent. These do not contain free aldehydic or ketonic group with $-OH$ group on the adjacent to carbonyl group
e.g. Sucrose is non-reducing sugar

- The linkage between two monosaccharide units through O atom is called **glycosidic linkage**

Haworth projection formulae



In β -form
OH is up
-H is down



In β -form
OH is up
-CH₂OH is down

The pairs of optical isomers which differ in the configuration only around C₁ are **anomers**

- Starch is polymer of α -D-glucose units and consists of two components
 - amylose
 - amylopectin
- Cellulose: polysaccharide of β -D-glucose units joined together by 1, 4-glycosidic linkage

Amino acids

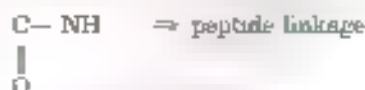


- acidic character is due to -COOH group
- basic character is due to -NH₂ group

Isoelectric point = pH at which there is no net charge

Peptides

Peptides are compounds formed by the condensation of two or more α -amino acids.



Denaturation of proteins A process which changes the physical and biological properties of proteins. The denaturation is caused by changes in temperature, pH etc.

- denaturation causes change in secondary and tertiary structures but primary structure remains intact
- coagulation of egg white on boiling, curdling of milk, formation of cheese

PROTEINS: Polymers of amino acids held by peptide (-CO-NH-) linkages

Fibrous proteins polypeptide chains are parallel and are held by hydrogen and disulphide bonds. Fibrous structure

- keratin, myosin, fibrous

Globular proteins polypeptide chains coil around to give a spherical shape.

- insulin, albumin

Structure of proteins

- Primary structure** gives the sequence in which α -amino acids are held together in a protein.
- Secondary structure** gives the manner in which the polypeptide chains are folded or arranged. These are of two types.
 - α -helix structure
 - β -pleated structure
- Tertiary structure** arises due to folding, coiling and bending of polypeptide chains giving three dimensional shapes. Two major shapes are fibrous proteins and globular proteins.
- Quaternary structure** gives the sub-units and their spatial arrangement with respect to each other.

$$\text{C. } \underset{\text{Alkane}}{\text{H}_7\text{O}_1} + \text{H}_7\text{C} \xrightarrow{\text{Malic acid}} \underset{\text{Alkane}}{\text{C}_{10}\text{H}_{17}\text{O}_1}$$

- phenylalanine hydroxylase causes disease phenylketonuria
- lysosomal cause disease subunit
- Enzyme streptokinase is used to dissolve blood clot to prevent heart attacks

Stetund

- Testosterone
- Estrogens
- Progesterone
- Cortisone

Peptide

- **hypernatremia**
- **hyperosmolality**
- **hypernatremia**

Amplitude

- Adrenalin
- Tyrosine

- Insulin produced in pancreas controls the glucose level in the blood.
- Thyroxine produced in thyroid glands controls metabolism of carbohydrates, acids and proteins.

Fat soluble: A, D, E and K stored in liver and adipose fat storing tissues.

- ↳ The deficiency of vitamins causes diseases.

Vitamin	Chemical name	Disease
A	Retinol	Night blindness or xerophthalmia
B ₁	Thiamine	Beri-beri
B ₂	Riboflavin	Pellagra, Digestive disorders
B ₆	Pyridoxine	Dermatitis, convulsions
B ₁₂	Cyanocobalamin	Pernicious anaemia
C	Ascorbic acid	Scurvy
D	Ergocalciferol	Rickets
E	Tocopherol	Stearity
K	Phylloquinone	Hæmophilia
H	Biotin	Dermatitis

Deoxyribonuclei und
DNA

Substrate and RNA

Narlentide

Nitrogenous base

- Principles

- * Urea (U)
- * Cytosine (C)

Pro 11:4

- Adenine A
- Hydroxyl

Sugar

- Deoxyriboses
- Riboses

Phosphate group



The two strands of DNA are held together by hydrogen bonds. Thymine and adenine are joined by two H bonds and cytosine and guanine by three H bonds.

Adenine Thymine
Guanine Cytosine



Signal: RNA nucleosides
as ribose and in DNA as
deoxyribose

- A, U G and U in RNA
- A, C, G and T in DNA



The polymers of nucleotides are **NUCLEIC ACIDS**

Nucleotides are joined together by phosphodiester linkages between 5' and 3' carbon atoms of pentose sugar.

Ans. Hydrogen bonding between NH and $\text{C}=\text{O}$ groups of peptide bonds stabilises the α -helix structure. Refer Text Page 30

Q.15. Differentiate between globular and fibrous proteins.

Ans. Refer Text Page 29.

Q.16. How do you explain the amphoteric behaviour of amino acids? (Kerala S.B. 2017)

Ans. Due to dipolar or zwitter ion structure, amino acids are amphoteric in nature. The acidic character of the amino acids is due to the NH_3^+ group and the basic character is due to the COO^- group as shown below

Acidic character



Basic character



Q.17. What are enzymes?

Ans. The enzymes are biological catalysts produced by the living cells which catalyse biochemical reactions in living organisms. Chemically enzymes are naturally occurring simple or conjugate proteins. For example, maltase, amylase, invertase, etc.

Q.18. What is the effect of denaturation on the structure of proteins?

Ans. During denaturation, the protein molecule moves from an ordered and specific conformation into a more random conformation. Denaturation does not change the primary structure of protein but results from a rearrangement of secondary and tertiary structures.

Q.19. How are vitamins classified? Name the vitamin responsible for the coagulation of blood.

Ans. Refer Text Pages 38 and 40

Vitamin responsible of coagulation of blood is vitamin K.

Q.20. Why are vitamin A and vitamin C essential to us? Give their important sources. / (H.P.S.B. 2017)

Ans. Refer Text Pages 38 and 39)

Q.21. What are nucleic acids? Mention their important functions.

Ans. Refer Text Page 41.

Two functions of nucleic acids are

i. Replication ii. Protein synthesis

Refer Section Pages 47 and 48).

Q.22. What is the difference between a nucleoside and a nucleotide?

Ans. A nucleoside contains only two basic components of nucleic acids namely a pentose sugar and a nitrogenous base. A nucleotide contains all the three basic components of nucleic acids namely a phosphoric acid group, a pentose sugar and a nitrogenous base.



Q.23. The two strands in DNA are not identical but are complementary. Explain.

Ans. The bases of one strand of DNA are paired with bases of other strand through hydrogen bonding. The hydrogen bonding is very specific because structures of heterocycles allow only one mode of pairing. The two strands of DNA are complementary to each other because the sequence of bases in one strand automatically determines that of the other.

Q.24. Write the important structural and functional differences between DNA and RNA.

Ans. Refer Text Pages 45 and 48

Q.25. What are different types of RNA found in the cell?

Ans. The different types of RNA found in the cells are

- | | |
|--------------------|-------|
| i. messenger RNA | m RNA |
| ii. transfer RNA | t RNA |
| iii. ribosomal RNA | r RNA |



NCERT

Exemplar Problems

Subjective Questions

Note: Objective Questions from Exemplar Problems are given in Competition File, page 88

Short Answer Type Questions

Q.1. Name the sugar present in milk. How many monosaccharide units are present in it? What are such oligosaccharides called?

Ans. Lactose is present in milk. It has two monosaccharide units glucose and galactose. These are called disaccharides.

Q.2. How do you explain the presence of all the six carbon atoms in glucose in a straight chain?

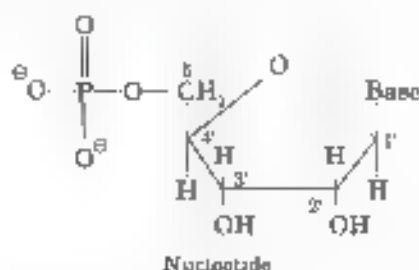
Ans. On prolonged heating with HI, glucose gives n-hexane.



This suggests that all the six carbon atoms are in a straight chain.

8. In nucleoside a base is attached at 1' position of sugar moiety. Nucleotide is formed by linking of phosphoric acid unit to the sugar unit of nucleoside. At which position of sugar unit is the phosphoric acid linked in a nucleoside to give a nucleotide?

Ans. Phosphoric acid is linked at 5' position of sugar moiety of nucleoside to form a nucleotide

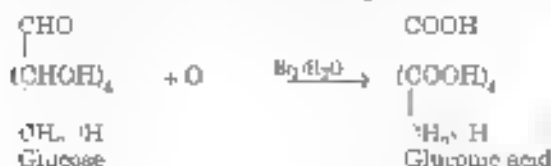


4. Name the linkage connecting monosaccharide units in polysaccharides.

Ans. Glycosidic linkage

5. Under what conditions glucose is converted to gluconic and saccharic acid?

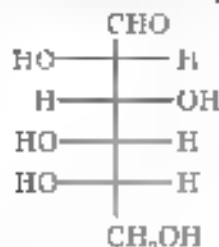
Ans. Glucose is converted to gluconic acid by Br_2 water and to saccharic acid by conc. HNO_3 .



8. Monosaccharides contain carbonyl group hence are classified, as aldose or ketose. The number of carbon atoms present in the monosaccharide molecule are also considered for classification. In which class of monosaccharide will you place fructose?

Ans. Fructose is a ketohexose.

7. The letters 'D' or 'L' before the name of a stereoisomer of a compound indicate the correlation of configuration of that particular stereoisomer. This refers to their relation with one of the isomers of glyceraldehyde. Predict whether the following compound has 'D' or 'L' configuration.



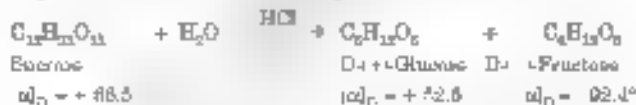
Ans. L configuration

8. Aldopentoses named as ribose and 2-deoxyribose are found in nucleic acids. What is their relative configuration?

Ans. D configuration

9. Which sugar is called invert sugar? Why is it called so?

Ans. Sucrose is called invert sugar. The sugar obtained from sugar beet is a colourless, crystalline and sweet substance. It is very soluble in water and its aqueous solution is dextrorotatory having $[\alpha]_D^{20} = +66.5^\circ$. On hydrolysis with dilute acids or enzyme invertase, cane sugar gives equimolar mixture of D-(-)-glucose and D-(+)-fructose



So, sucrose is dextrorotatory but after hydrolysis, gives dextrorotatory glucose and laevorotatory fructose. D-(-)-fructose has a greater specific rotation than D-(-)-glucose. Therefore the resultant solution upon hydrolysis is laevorotatory in nature with specific rotation of -19.9° . Since there is change in the sign of rotation from dextro before hydrolysis to laevo after hydrolysis, the reaction is called inversion reaction and the mixture 'glucose and fructose' is called invert sugar.

10. Amino acids can be classified as α -, β -, γ -, δ - and so on depending upon the relative position of amino group with respect to carboxyl group. Which type of amino acids form polypeptide chain in proteins?

Ans. α -amino acids. $\text{R}-\text{CH}-\text{COOH}$

11. α -Helix is a secondary structure of proteins formed by twisting of polypeptide chain into right handed screw like structures. Which type of interactions are responsible for making the α -helix structure stable?

Ans. In α -helix, a polypeptide chain is stabilised by the formation of hydrogen bonds between $\text{NH}-$ group of amino acids in one turn with the $>\text{C}=\text{O}$ groups of amino acids belonging to adjacent turn.

12. Some enzymes are named after the reaction, where they are used. What name is given to the class of enzymes which catalyse the oxidation of one substrate with simultaneous reduction of another substrate?

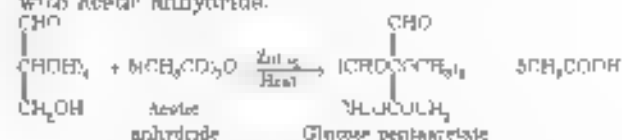
Ans. Oxidoreductase

13. During curdling of milk, what happens to sugar present in it?

Ans. Lactose changes to lactic acid.

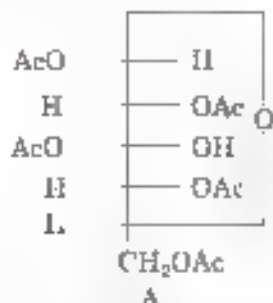
14. How do you explain the presence of five $-\text{OH}$ groups in glucose molecule?

Ans. Glucose gives pentaacetate derivative on acetylation with acetic anhydride.

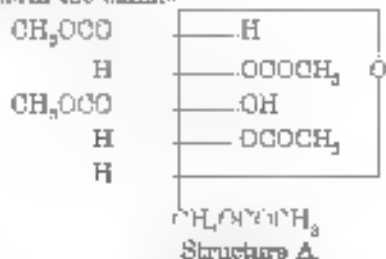


This confirms the presence of five $-\text{OH}$ groups

15. Why does compound (A) given below not form an oxime?



Ans. Glucose pentacetate structure A does not have a free -OH group at C1 and therefore, cannot be converted to the open chain form to give -CHO group hence it does not form the oxime.



16. Why must vitamin C be supplied regularly in diet?

Ans. Vitamin C is water soluble and therefore, excess of it is readily excreted in urine. Hence, it cannot be stored in our body.

17. Sucrose is dextrorotatory but the mixture obtained after hydrolysis is laevorotatory. Explain.

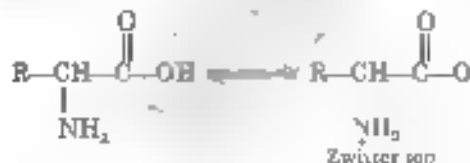
Ans. Sucrose is dextrorotatory having $[\alpha]_D^{20} = +66.5^\circ$. On hydrolysis with dilute acids or enzymes it gives equimolar D-+glucose and D-+fructose.



Since D-+fructose has larger specific rotation than D-+glucose the resulting mixture has specific rotation of -39.0° . Therefore, the mixture is laevorotatory.

18. Amino acids behave like salts rather than simple amines or carboxylic acids. Explain.

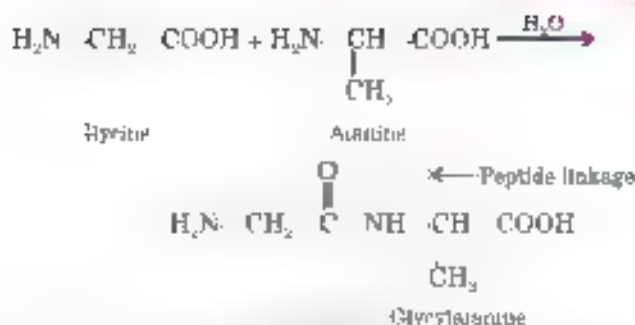
Ans. In aqueous solution, the carboxyl group loses a proton and amino group accepts a proton to form a dipolar ion or zwitter ion.



19. Structures of glycine and alanine are given below. Show the peptide linkage in glycylalanine.



Ans. In glycylalanine carboxyl group of glycine combines with the amino group of alanine forming a dipeptide as:



20. Protein found in a biological system with a unique three-dimensional structure and biological activity is called a native protein. When a protein in its native form is subjected to a physical change like change in temperature or a chemical change like change in pH, denaturation of protein takes place. Explain the cause.

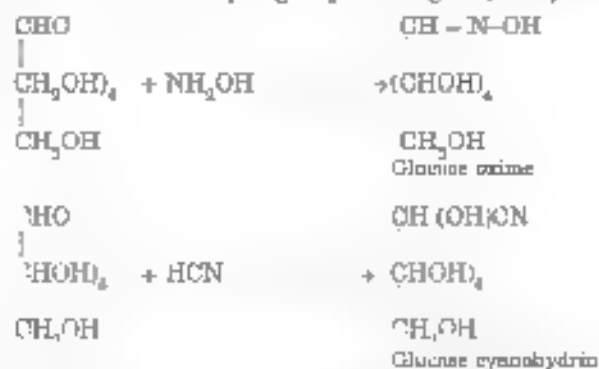
Ans. Due to physical or chemical change, the hydrogen bonds in proteins are disturbed, the protein molecules uncoil from an ordered and specific conformation into a more random conformation. As a result, the protein loses its biological activity. This is called denaturation of proteins.

21. Activation energy for the acid catalysed hydrolysis of sucrose is 6.22 kJ mol^{-1} , while the activation energy is only 2.15 kJ mol^{-1} when hydrolysis is catalysed by the enzyme sucrase. Explain.

Ans. Enzymes act as biocatalysts and reduce the magnitude of activation energy by providing alternative path. In the hydrolysis of sucrose the enzyme sucrase reduces the activation energy from 6.22 kJ mol^{-1} to 2.15 kJ mol^{-1} .

22. How do you explain the presence of an aldehydic group in a glucose molecule?

Ans. Glucose reacts with hydroxylamine to form a monoxime and adds one molecule of hydrogen cyanide to give cyanohydrin.



Therefore, it contains a carbonyl group which can be an aldehyde or a ketone. On mild oxidation with bromine water, glucose gives gluconic acid which is a carboxylic acid containing six carbon atoms.



This indicates that carbonyl group present in glucose is an aldehydic group.

23. Which moieties of nucleosides are involved in the formation of phosphodiester linkages present in dinucleotides? What does the word di-ester in the name of linkage indicate? Which acid is involved in the formation of this linkage?

Ans. When nucleoside is linked to phosphoric acid at 5'-position of sugar moiety, we get a nucleotide. Nucleotides are joined together by phosphodiester linkage between 5' and 3' carbon atoms of the pentose sugar.

24. What are glycosidic linkages? In which type of biomolecules are they present?

Ans. The linkage between two monosaccharide units through oxygen atom is called glycosidic linkage. It is present in disaccharides and polysaccharides.

25. Which monosaccharide units are present in starch, cellulose and glucose and which linkages link these units?

Ans. In starch α -glucose units are present in cellulose β -D glucose units are present. In starch and glycogen, glycosidic α -linkage is present and in cellulose glycosidic β -linkage is present between glucose units.

26. How do enzymes help a substrate to be attacked by the reagent effectively?

Ans. Active site of enzymes hold the substrate molecule in a suitable position, so that it can be attacked by the reagent effectively.

27. Describe the term D- and L- configuration used for amino acids with examples.

Ans. The sugars are divided into two families the *D-family* and *L-family* which have definite configurations. These configurations are represented with respect to glyceraldehyde as the standard. The glyceraldehyde may be presented by two forms as



D- (+)-glyceraldehyde L- (-)-glyceraldehyde

The D-configuration has -OH attached to the carbon adjacent to -CHO, H on right while L-configuration has -H attached to the carbon adjacent to -CHO, OH on left. The sugars are called D- or L- depending upon whether the configuration of the molecule is related to D-glyceraldehyde or L-glyceraldehyde. It has been found that all naturally occurring sugars belong to D-series e.g. D-glucose, D-ribose and D-fructose.

28. How will you distinguish 1° and 2° hydroxyl groups present in glucose? Explain with reactions.

Ans. On oxidation with HNO_3 , glucose as well as gluconic acid, both give a dicarboxylic acid, saccharic acid. This indicates the presence of a primary alcoholic (-OH) group in glucose. The other -OH groups are secondary.



29. Coagulation of egg white on boiling is an example of denaturation of protein. Explain in terms of structural changes.

Ans. Coagulation of egg white on boiling is an example of denaturation. This is because when a protein is subjected to physical change in temperature. The hydrogen bonds are disturbed. Due to this, globules unfold and helix get uncoiled and protein loses its biological activity.



QUICK

MEMORY TEST



A. Say True or False

- Both glucose and fructose are reducing sugars.
- Lecithin is an α -amino acid.
- Starch has the components amylose and amylopectin.
- Chemically denaturation does not change the primary structure of proteins.
- The disease albinism is caused by the deficiency of enzyme tyrosinase.
- Uracil occurs in DNA and not in RNA.
- Lactose on hydrolysis with acids gives galactose and fructose.
- Glycogen is a polymer of glucose units.
- α -Amino acids show basic character due to $-\text{COO}^-$ group and acidic character due to $-\text{NH}_3^+$ group.
- Both glucose and fructose form the same osazone.
- The synthesis of proteins is governed by DNA.
- When glucose is heated with methanol in the presence of dry HCl gas, it forms one methyl glucoside.
- Alanine and valine are neutral α -amino acids.

- Keratin, fibron and collagen are fibrous proteins.
- Deficiency of vitamin D causes rickets.

B. Complete the missing links

- The sugar in DNA is _____.
- Cellulose is a linear polymer of _____.
- Amylopectin is a polymer of _____.
- The acidic character of glycine is due to _____ group.
- Deficiency of _____ causes scurvy.
- A chemical or physical change that alters the sequence of bases in DNA molecule is called _____.
- Heart attacks can be checked by using the enzyme _____.
- The chemical name of vitamin B_{12} is _____.
- The base _____ is found only in the nucleotides of RNA.
- The two strands of the double helix of DNA are held together at definite distances through _____.
- Most of the naturally occurring _____ have D-configuration while most of the naturally occurring _____ have L-configuration.

12. Starch is hydrolysed by enzyme α -amylase to maltose
13. In RNA, the sugar is ribose and in DNA, the sugar is deoxyribose
14. Denaturation involves conversion of α -helix proteins to random coil
15. The molecule in which one of the nitrogen bases is bonded with a sugar molecule is called nucleoside

A. Choose the correct alternative

1. Glucose and fructose form same/different osazone.
2. DNA/RNA controls the transmission of hereditary effects
3. The chemical name of vitamin B₂ is riboflavin/cyanocobalamin
4. The disease xerophthalmia is caused by deficiency of vitamin D/vitamin A
5. Leucine/aspartic acid is essential amino acid

6. The acidic character of glycine is due to COO^- group/ NH_3^+ group
7. Pairing of thymine with adenine occurs through three/two hydrogen bonds
8. Thymine is present only in RNA/DNA
9. Guanine is a purine/pyrimidine
10. The conversion of sucrose to glucose and fructose is carried out by amylase/invertase enzymes.
11. Denaturation alters/does not alter primary structure of proteins
12. Collagen is a fibrous/globular protein.
13. At isoelectric point the amino acids have least/maximum solubility in water
14. α -D-glucose and β -D-glucose are anomers/enomers.
15. Amylopectin is water soluble/insoluble fraction

Answers

Quick

MEMORY TEST



A. Say True or False

1. True
2. False
3. True
4. True
5. True
6. False. Uracil is present in RNA and not in DNA.
7. False. Lactose on hydrolysis gives glucose and galactose.
8. True
9. True
10. True
11. False. RNA governs the synthesis of proteins.
12. False. Glucose forms two isomeric methylglycosides, methyl α -D-glucoside and methyl β -D-glucoside.
13. True. Because they contain equal number of amino and carboxyl groups.
14. True
15. True

B. Complete the missing links

- | | |
|---------------------------|-----------------------|
| 1. deoxyribose | 2. β -D-glucose |
| 3. α -D-glucose | 4. NH_3^+ |
| 5. vitamin C | 6. mutation |
| 7. streptokinase | 8. cyanocobalamin |
| 9. ascorbic acid | 10. hydrogen bonding |
| 11. sugars, amino acids | 12. amylase |
| 13. ribose, 2-deoxyribose | 14. globular, fibrous |
| 15. nucleoside | |

C. Choose the correct alternative

- | | |
|--------------------|--------------------------|
| 1. same | 2. DNA |
| 3. riboflavin | 4. vitamin A |
| 5. leucine | 6. NH_3^+ group |
| 7. three | 8. DNA |
| 9. purine | 10. invertase |
| 11. does not alter | 12. fibrous |
| 13. least | 14. anomers |
| 15. insoluble | |

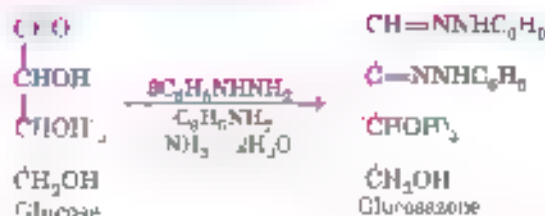
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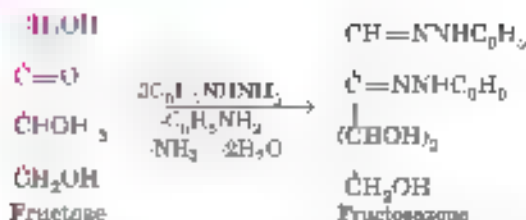
Higher Order Thinking Skills & Advanced Level

QUESTIONS WITH ANSWERS

Q.1. Glucose and fructose give the same osazone. Explain.

Ans. The osazone formation involves the reaction at C₁ and C₂ carbon while the rest of the molecule remains intact. Since glucose and fructose differ from each other only in the arrangement of atoms C₁ and C₂, therefore, they give the same osazone as shown





Q.3. What forces are responsible for the stability of α -helix. Why is it also known as 3.6₁₃ helix?

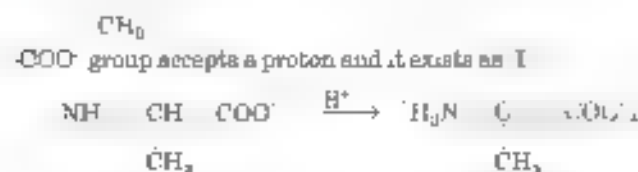
Ans. The stability of α -helix structure is due to intramolecular hydrogen bonding between NH and CO groups of the polypeptide chain. The α -helix is also known as 3.6₁₃ because each turn of α -helix contains approximately 3.6 amino acids and a 13-membered ring is formed by hydrogen bonding.

Q.3. Alanine has the structure $\text{NH}_2-\text{CH}-\text{COOH}$.

Write its structure at pH = 2 and pH = 10.

Ans. Alanine exists as a Zwitter ion in aqueous solution as

$\text{NH}_3^+ - \text{CH} - \text{COO}^-$. In presence of acid (pH = 2), the basic



In basic medium (pH = 10), the acidic group NH_3^+ gives a proton to the base and it exists as II



Q.4. Glucose shows mutarotation when it dissolves in water. The specific rotation of α -D-glucose and β -D-glucose is $+112.2^\circ$ and $+18.7^\circ$ respectively. Calculate the percentage of two anomers present at equilibrium mixture with a specific rotation of $+52.6^\circ$

Ans. Let percentage of α -D-glucose present at equilibrium = x

If the amount of open-chain form present at equilibrium is assumed to be negligible, then

percentage of β -D-glucose present at equilibrium = $100 - x$

$$\frac{112.2 \times x + 18.7 \times (100 - x)}{100} = 52.6$$

$$112.2x + 1870 - 18.7x = 5260$$

$$93.5x = 3390$$

$$x = 36.3\%$$

$$\% \text{ of } \alpha\text{-D-glucose} = 36.3\%$$

$$\% \text{ of } \beta\text{-D-glucose} = 100 - 36.3 = 63.7\%$$

Q.5. The Chargoff's rule says that DNA contains equal amounts of guanine and cytosine and also equimolar amounts of adenine and thymine as:

$$G = C \text{ and } A = T$$

(a) Does Chargoff's rule imply that equal amounts of guanine and adenine are present in DNA?

(b) Does Chargoff's rule imply that the sum of purine residues equals the sum of pyrimidine residues i.e. does $A + G = C + T$?

(c) Does Chargoff's rule apply only to double stranded DNA or would it apply to each individual strand if the double helical strand were separated into two complementary strands?

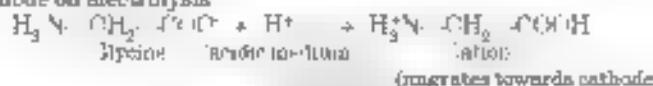
Ans. (a) No, it does not imply that $G = A$

(b) Yes, it implies that $A + G = C + T$

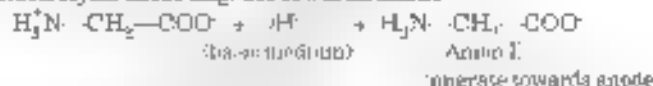
(c) This rule applies only to double stranded DNA

Q.6. Explain. On electrolysis in acidic solution, glycine migrates towards cathode while in alkaline solution, it migrates towards anode.

Ans. Glycine exists as Zwitter ion, $^+\text{NH}_3-\text{CH}_2-\text{COO}^-$. In acidic solution, it exists as cation I, which migrate towards cathode on electrolysis



In alkaline solution, glycine exists as anion II and therefore, on electrolysis these migrate towards anode



Q.7. Glucose forms an oxime but glucose pentaacetate does not. Explain.

Ans. Glucose reacts with NH_2OH via open chain form which has free $\text{C}=\text{O}$ group and forms oxime. On the other hand,

glucose pentaacetate cannot be converted to open chain form because if a anomeric hydroxyl group $\text{C}(\text{OH})_1$ is acetylated and therefore, cannot form oxime

Q.8. The K_a and K_b values of α -amino acids are very low. Explain.

Ans. The K_a and K_b values of α -amino acids are very low because in α -amino acids, the acidic group is NH_3^+ and not usual COOH group as in carboxylic acids and basic group is COO^- instead of NH_2 group in aliphatic amines. For example, the K_a and K_b values of glycine are

$$K_a = 1.6 \times 10^{-10} \text{ and } K_b = 2.4 \times 10^{-11}$$

Q.9. Give one example each of ω -amino acid which is achiral and α -amino acid having more than one chiral centre.

Ans. Achiral Glycine $^+\text{NH}_3\text{CH}_2\text{COO}^-$

Chiral Isoleucine, $\text{CH}_3\text{CH}_2\text{CH}(\text{NH}_3^+)\text{CH}(\text{COO}^-)\text{CH}_3$

Q.10. What is the smallest aldose which can form a cyclic hemiacetal? Which functional groups are involved in its formation?

Ans. The smallest aldose is a tetrose which has four C atoms and an O to form a five membered ring

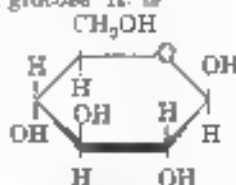
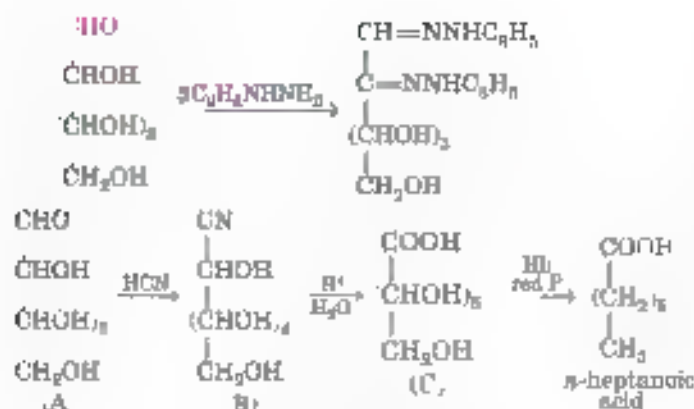
The CHO and primary OH groups are incorporated in the ring.

Q.11. Do the anomers of α -D-glucose have specific rotations of the same magnitude but opposite signs?

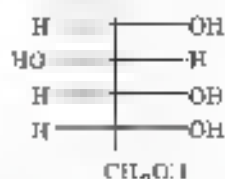
Ans. No, only enantiomers have this characteristic property and anomers are not enantiomers

Q.12. A compound A ($\text{C}_6\text{H}_{12}\text{O}_6$) is oxidised by bromine water into monobasic acid. It also reduces Tollen's reagent and reacts with HCN to give a compound (B) which on hydrolysis gives a compound (C). On treating C with HI /red P, n -heptanoic acid is obtained. Compound A on treatment with excess phenyl hydrazine gave D-glucosazone. Name the compound A and draw its cyclic form.

Ans. The compound A gives Tollen's reagent and is oxidised to monobasic acid with bromine water. It gives D-glucosazone with excess phenyl hydrazine. It must be glucose as



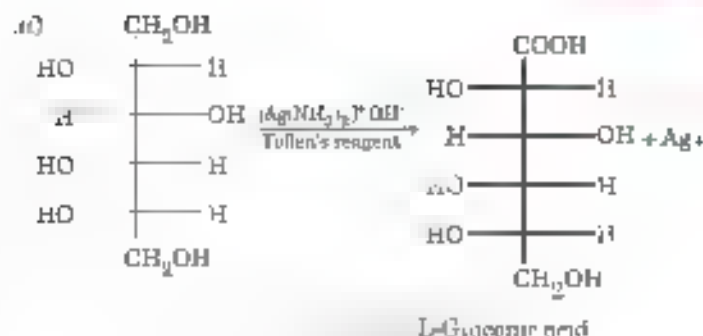
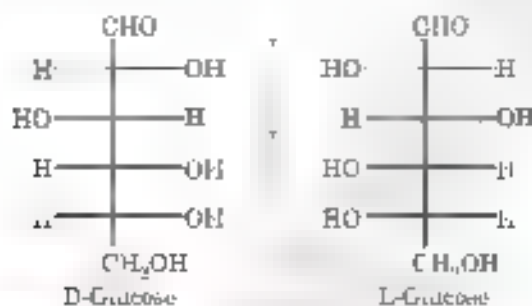
Q.13. The Fischer projection of D-glucose is



(i) Write Fischer projection for L-glucose.

(ii) Give the product of reaction of L-glucose with Tollen's reagent.

Ans. (i) The Fischer projection of L-glucose is mirror image of D-glucose.



Q.14. Predict towards which electrode would an α -amino acid migrate in an electric field at a

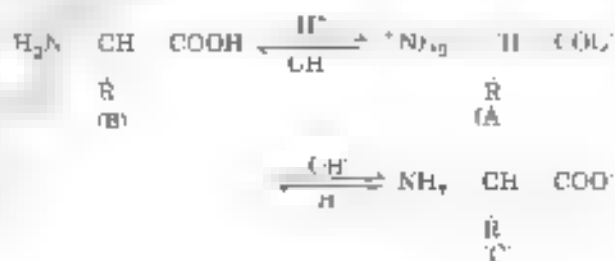
(i) $\text{pH} < \text{pI}$ (ii) $\text{pH} > \text{pI}$ and (iii) $\text{pH} = \text{pI}$. Explain

Ans. At isoelectric point, $\text{pI} = \text{pH}$, there is no net charge on α -amino acid and it does not migrate under electric field.

i. Below the pI ($\text{pH} < \text{pI}$), the cation B predominates and therefore, it migrates towards cathode.

ii. Above the pI ($\text{pH} > \text{pI}$), the anion C predominates and therefore, it migrates towards anode.

iii. At $\text{pH} = \text{pI}$ there is no net charge and it does not migrate



Q.15. If one of the strands of DNA has the following sequence of bases running in the 5'→3' direction :



(i) What is the sequence of bases in the complementary strand?

(ii) Which base is closest to the 5'—end in the complementary strand.

Ans. i. Sequence of bases in complementary strand



ii. Guanine



Revision Exercises

Very Short Answer Questions carrying 1 mark

- What is mutarotation? *[H.P.S.B. 2005 P.B.S.B. 2017]*
- What is the basic difference between proteins and polypeptides?
- What type of bonding occurs in α -helix configuration?
- Name the enzyme which is used to cure the heart disease.
- Name the enzyme whose deficiency causes albinism and phenylketonuria.
- What do we get when starch is hydrolysed?

- Name the vitamin whose deficiency causes (i) night blindness and (ii) poor coagulation of blood.

8. What do you understand by glycosidic linkage?

[H.P.S.B. 2016]

9. What is peptide linkage?

[H.P.S.B. 2016]

10. Why is cellulose not digestible in human beings?

[Hr.S.B. 2009]

11. Which sugar molecule is present in DNA molecule ?
Pb.S.B. 2013
12. Which sugar molecule is present in RNA molecule ?
Pb.S.B. 2019
13. Write the chemical name of vitamin B₁₂.
Mizoram S.B. 2012
14. What is the chemical name of vitamin C and which disease is caused by its deficiency? *Pb. S.B. 2018, 2018*
15. What is the chemical name of vitamin B₁ and which disease is caused by its deficiency? *(Pb. S.B. 2016)*
16. What is the chemical name of vitamin A and which disease is caused by its deficiency? *Pb. S.B. 2013, 2016*
17. What is the basic difference between starch and cellulose?
Pb. S.B. 2015
18. Name the enzyme which converts glucose into alcohol.
Pb. S.B. 2014 and H.P. S.B. 2015
19. Name the enzyme which converts starch into maltose ?
Pb. S.B. 2014
20. What is the difference between nucleoside and nucleotide?
Pb. S.B. 2015, 2017
21. Which of the two components of starch is water soluble ?
D.S.B. 2014
22. Which component of starch is a branched polymer of α -glucose and insoluble in water ?
(D.S.B. 2014)
23. Name two bases present in DNA. *Assam S.B. 2017*
24. Which α -amino acid is not optically active ?
Meghalaya S.B. 2018
25. Deficiency of which vitamin causes the disease 'Rickets'?
Karnataka S.B. 2018

CBSE QUESTIONS

26. What is meant by reducing sugar ? *(A.I.S.B. 2008)*
27. What are monosaccharides ? *(A.I.S.B. 2010, Pb.S.B. 2017)*
28. Write the structure of the product obtained when glucose is oxidised with nitric acid. *(A.I.S.B. 2012)*
29. Write a reaction which shows that all the carbon atoms in glucose are linked in a straight chain. *(A.I.S.B. 2012)*
30. Write the name of linkage joining two amino acids.
A.I.S.B. 2018
31. What are the products of hydrolysis of lactose?
A.I.S.B. 2014
32. What are the products of hydrolysis of sucrose ?
A.I.S.B. 2014, D.S.B. 2014
33. What are the products of hydrolysis of maltose ?
A.I.S.B. 2014

MCQs from State Boards' Examinations

34. The linkage which holds various amino acid units in primary structure of proteins is
(a) glycosidic linkage (b) hydrogen bond
(c) peptide linkage (d) ionic bond
Meghalaya S.B. 2013
35. Vitamin A is called
(a) Ascorbic acid (b) Retinol
(c) Nicotinic acid (d) Tocopherol *Hr. S.B. 2014*
36. The deficiency of vitamin B₁ causes which disease ?
(a) Beri-Beri (b) Rickets
(c) Anemia (d) Kerosin *(Hr. S.B. 2014)*
37. Deficiency of vitamin C causes
(a) Scurvy (b) Rickets
(c) Anemia (d) None of these
Hr. S.B. 2014
38. An example of non-reducing sugar is
(a) Sucrose (b) Lactose
(c) Maltose (d) None *(Hr. S.B. 2014)*
39. Which of the following is not an essential amino acid ?
(a) Glycine (b) Lysine
(c) Phenyl alanine (d) Valine *Hr. S.B. 2014*
40. Which of following is water soluble vitamin ?
(a) Vitamin E (b) Vitamin K
(c) Vitamin B (d) Vitamin A
Hr. S.B. 2014, Mizoram S.B. 2017, Kerala S.B. 2018
41. Vitamin B₁ is
(a) Riboflavin (b) Cobalamin
(c) Thiamine (d) Pyridoxine *J & K S.B. 2015*
42. Which is sweetest of the following.
(a) Sucrose (b) Glucose
(c) Fructose (d) Maltose *J & K S.B. 2015*
43. Rickets may be caused by the deficiency of which vitamin?
(a) Vitamin D (b) Vitamin C
(c) Vitamin A (d) Vitamin B *Hr. S.B. 2015*
44. The function of enzymes in the living system is to
(a) maintain pH (b) catalyse biochemical process
(c) provide immunity (d) transport oxygen
Meghalaya, S.B. 2018
45. The disaccharide present in milk is
(a) sucrose (b) maltose
(c) lactose (d) cellulose
Nagaland S.B. 2016
46. Which base is present in RNA but not in DNA ?
(a) Uracil (b) Cytosine
(c) Guanine (d) Thymine
Meghalaya S.B. 2017, Hr. S.B. 2018
47. In aqueous solution, an amino acid exists as
(a) cation (b) anion
(c) dianion (d) zwitter ion
Meghalaya S.B. 2017
48. Which of the following is stored in liver of animals?
(a) Amylose (b) Cellulose
(c) Amylopectin (d) Glycogen *Hr. S.B. 2017*
49. Which of the following is a polysaccharide?
(a) Maltose (b) Sucrose
(c) Fructose (d) Cellulose *(Kerala S.B. 2017)*

50. The Vitamin responsible for the coagulation of blood is
(a) Vitamin B₁ (b) Vitamin D
(c) Vitamin K (d) Vitamin C
Hr S.B. 2018
51. Which one is the complimentary base of adenine in one strand to that in the other strand of DNA?
(a) Cytosine (b) Guanine
(c) I am (d) Thymine
Mizoram S.B. 2018
52. Ribose is a
(a) monosaccharide (b) polysaccharide
(c) polypeptide (d) disaccharide
Nagaland S.B. 2018
53. In which of the following order base, phosphate and sugar are arranged in the nucleotide of DNA?
(a) Base-phosphate-sugar (b) Base-sugar-phosphate
(c) Phosphate-base-sugar (d) Sugar-base-phosphate
West Bengal S.B. 2018

Short Answer Questions (Carrying 2 or 3 marks)

- What are monosaccharides? Draw open chain structure of aldopentose and aldohexose. How many asymmetric carbons are present in each?
- What are reducing and non-reducing sugars? What is the structural features characterizing reducing sugars?
- Distinguish between
(i) a globular protein and fibrous protein
Nagaland S.B. 2015, H.P.S.B. 2015, Kerala S.B. 2018, Hr S.B. 2018
(ii) α -glucose and β -glucose
Hr S.B. 2018
(iii) primary and secondary structure of protein.
Nagaland S.B. 2016, H.P.S.B. 2015
(iv) DNA and RNA
Nagaland S.B. 2016, H.P.S.B. 2015
(v) Nucleoside and nucleotide
Pb S.B. 2015
- a. Explain zwitter ion with example
b. Write the chemical name of vitamin C and name the disease caused by the deficiency of vitamin C
H.P.S.B. 2017
- What type of forces are responsible for the formation of
(a) Cross linking of polypeptide chains
(b) α -helix formation
(c) β -sheet structure.
- What are enzymes? How do enzymes differ from ordinary chemical catalysts? Comment on the specificity of enzyme action. What is the most important reason for their specificity?
- Name two components of starch. How do they differ from each other structurally? *C.B.S.E. Sample paper 2007*
- (a) What are essential amino acids?
(b) Acetubhydrate ($C_{12}H_{22}O_{11}$) is boiled with $40\% H_2SO_4$ in alcoholic solution to form two hexoses with the same chemical formula. Identify the carbohydrate and the two hexoses. Give necessary chemical equations.
(c) What is denaturation of protein? *Assam S.B. 2018*
- a. What are vitamins? Name any two vitamins.
b. Why vitamin A and C are essential to us? Name one important source of each. *Hr S.B. 2017*
- a. List the important structural and functional differences between DNA and RNA. *H.P.S.B. 2016, Pb S.B. 2018*
b. Draw the structure of β -D-ribose and β -D-2-deoxyribose
Hr S.B. 2011
- a. What are essential and non-essential amino acids?
b. Give chemical name of vitamin-A.
c. Name the enzyme which converts glucose into ethanol.
H.P.S.B. 2018
- a. What is essentially the difference between α -form of glucose and β -form of glucose? What is meant by pyranose structure of glucose? *Hr S.B. 2018*
b. Describe what you understand by primary and secondary structure of proteins. *D.S.B. 2011*
- a. What is meant by a) a peptide linkage b) a glycosidic linkage?
b. Name the bases present in RNA. Which one of these is not present in DNA? *D.S.B. 2011*
- a. Write two differences between starch and cellulose
b. Write one function and two sources of vitamin D
Pb.S.B. 2013
- a. Name the metal present in Vitamin-B₁₂
b. What is Zwitter ion?
c. Name the metal present in green leaves.
H.P.S.B. 2018
- Define the following terms
(a) Anomers
(b) Peptide bond
(c) Reducing sugar
Hr.S.B. 2018
- (a) What is denaturation of proteins?
b. What type of bonds hold a DNA double helix together?
c. Which enzyme is present in saliva? What is its function?
H.P.S.B. 2018
- a. What is meant by
(i) peptide linkage (ii) isocatalysis? *(D.S.B. 2012)*
b. Write any two reactions of glucose which cannot be explained by the open chain structure of glucose molecule
D.S.B. 2013
- a. What are globular and fibrous proteins? Give examples
b. What is glycosidic linkage? Name the disease caused by the deficiency of vitamin D. Give one function of vitamin D
Nagaland S.B. 2018
- (i) Write the reaction of glucose with HI
(ii) What is glycogen? Why is it called animal starch?
(iii) Name the vitamin responsible for the coagulation of blood
Meghalaya S.B. 2013
- a. Write Haworth structure of "Lactose"
b. (i) What are non-essential amino acids?
(ii) Write Zwitter ion structure of "glycine"
c. Name the nitrogenous base present in RNA but not in DNA.
Karnataka S.B. 2018
- a. Name one fibrous protein and one globular protein
b. What are the products obtained on hydrolysis of sucrose?
c. What is the structural feature characterising reducing sugars?
Meghalaya S.B. 2018

23. (a) Give one example each of disaccharide and a polysaccharide.
 (b) What are three types of RNA molecules which perform different functions? (D.S.B. 2015)
24. (a) (i) Name the water insoluble component of starch.
 (ii) Mention one water soluble vitamin.
 (iii) Is Lysine an essential or non-essential amino acid?
 (b) Write the structure of maltose. (Karnataka S.B. 2014)
25. Biomolecules are formed by certain specific linkages between simple monomeric units. Write the names of linkages and monomeric units in the following class of biomolecules.
 (i) Starch
 (ii) Protein
 (iii) Nucleic acid (Meghalaya S.B. 2014)
26. (i) Deficiency of which vitamin causes rickets?
 (ii) Give an example for each of fibrous protein and globular protein.
 (iii) Write the product formed on reaction of D-glucose with Br_2 water. (D.S.B. 2014)
27. (a) Explain primary and secondary structure of proteins.
 (b) Differentiate between RNA and DNA.
 (c) What is denaturation of proteins? (H.P.S.B. 2018)
28. Discuss in brief the primary, secondary and tertiary structure of proteins. (Mizoram S.B. 2015)
29. (a) What is glycosidic linkage?
 (b) What are nucleic acids? Mention their two important biological functions.
 Or
 Write the full form of DNA and RNA. Name the specific nitrogenous bases present in DNA and RNA. (Meghalaya S.B. 2015)
30. (a) What is denaturation of proteins?
 (b) What are carbohydrates? How are they classified?
 (c) Why are vitamins A and C are essential to us? Give their sources. (J.K. S.B. 2015)
31. (a) What are zwitter ions?
 (b) What is denaturation of proteins?
 (c) What is meant by inversion of sugar?
 (d) What is mutarotation? (HP S.B. 2015)
32. What happens when glucose reacts with the following
 (a) HI heat
 (b) NH_4OH
 (c) Br_2 water (Hr S.B. 2018)
33. (i) Which one of the following is a disaccharide: Starch, Maltose, Fructose, Glucose?
 (ii) What is the difference between fibrous protein and globular protein?
 (iii) Write the name of vitamin whose deficiency causes bone deformities in children. (D.S.B. 2015)
34. (i) What are carbohydrates? Give the important functions of carbohydrates.
 (ii) What is difference between α -glucose and β -glucose? Write their cyclic structures. (H.P. S.B. 2018)
35. What is meant by denaturation of protein? Differentiate between fibrous proteins and globular proteins.
 Or
 Name the three major classes of carbohydrates and give the distinctive characteristics of each class. (Hr S.B. 2018)
36. Explain the following terms in relation to proteins:
 (i) Peptide linkage (Hr S.B. 2016, Tripura S.B. 2018)
 (ii) Denaturation (Hr S.B. 2018)
37. (a) What is polysaccharide? Explain with an example.
 (b) What is meant by primary structure of proteins? (Kolkata S.B. 2016)
38. What are neutral, acidic and basic amino acids? Which vitamin deficiency lead to scurvy? Mention one function of vitamin C.
 Or
 What are reducing and non-reducing sugars? What is the sequence of bases on mRNA molecule that can be synthesised on the following strand of DNA-
 GATCATGGCT (Nagaland S.B. 2018)
39. Distinguish between the following
 (i) A globular protein and a fibrous protein.
 (ii) Primary and secondary structure of proteins. (Meghalaya S.B. 2018)
40. (a) (i) What is Zwitter ion?
 (ii) Name a source of vitamin E.
 (iii) Name the disease caused due to deficiency of vitamin K in our body.
 Or
 (b) (i) What are enzymes?
 (ii) What kind of linkages hold together monomers of DNA?
 (iii) What is denaturation of protein? (Assam S.B. 2018)
41. (i) Write the name of two monosaccharides obtained on hydrolysis of lactose sugar.
 (ii) Why Vitamin C cannot be stored in our body?
 (iii) What is the difference between a nucleoside and nucleotide? (D.S.B. 2018)
42. (a) Explain the terms.
 (i) Zwitter ion (ii) Oligosaccharides.
 Or
 (b) What are the different types of RNA found in the cells of an organism? State the functions of each type. (Nagaland S.B. 2017)
43. What is denaturation of proteins? Mention four different types of forces that stabilize protein structure. (Mizoram S.B. 2017)
44. Define the terms:
 (i) Biomolecules (ii) Carbohydrates
 (iii) Reducing Sugars. (Hr S.B. 2017)
45. (a) Fresh tomatoes are a better source of vitamin C than those which have been stored for some time. Why?
 (b) Represent sucrose and α -D-maltose in the form of Haworth structures. (Manipur S.B. 2017)
46. Explain the amphoteric behaviour of amino acids. (Kerala S.B. 2017)
47. (a) What are non-essential amino acids? Give one example.
 (b) Name one vitamin which is not soluble in water and fat.
 (c) What is the chemical basis of heredity? (Assam S.B. 2017)
48. (a) What are reducing sugars?
 (b) What is the effect of denaturation on the structure of proteins?
 (c) Why cannot vitamin C be stored in our body? (Meghalaya S.B. 2017)
49. What are monosaccharides? Give the reaction of glucose with acetic anhydride and hydroxylamine. (Jammu S.B. 2018)
50. What are carbohydrates? Write any four important functions of carbohydrates. (Mizoram S.B. 2018)

CBSE QUESTIONS

51. (a) Answer the following questions briefly
 (i) What are two good sources of vitamin A?
 (ii) What are nucleotides?
 (iii) Give an example of a simple lipid.
 b) How are carbohydrates classified? (A.I.S.B. 2007)
52. (a) Answer the following questions briefly
 i) What are reducing sugars?
 (ii) What is meant by denaturation of a protein?
 (iii) How is oxygen replenished in our atmosphere?
 b) Define enzyme. (A.I.S.B. 2007)
53. What happens when D-glucose is treated with the following reagents?
 (i) H_2
 (ii) Bromine water
 (iii) HNO_3 (A.I.S.B. 2008)
54. How are vitamins classified? Mention the chief sources of vitamins A and C. (A.I.S.B. 2008)
55. a) Name two water soluble vitamins, their sources and the diseases caused by their deficiency in diet. (D.S.B. 2009)
- b) Name the four bases present in DNA. Which one of these is not present in RNA? (A.I.S.B. 2009)
56. Name two fat soluble vitamins, their sources and the diseases caused due to their deficiency. (A.I.S.B. 2009)
57. Name the four bases present in DNA. Which one of these is not present in RNA? (A.I.S.B. 2010)
58. (a) What is meant by
 i) peptide linkage ii) pyranose structure of glucose.
 b) Write the main structural differences between DNA and RNA. Of the four bases present, name those which are common to both DNA and RNA. (A.I.S.B. 2011)
59. What is essentially the difference between α -glucose and β -glucose? What is meant by pyranose structure of glucose? (A.I.S.B. 2012)
60. Define the following terms as related to proteins
 (i) Peptide linkage
 (ii) Primary structure
 (iii) Denaturation (A.I.S.B. 2008, 2014, D.S.B. 2014)
61. Define the following terms
 (i) Glycosidic linkage
 (ii) Invert sugar
 (iii) Oligosaccharides (A.I.S.B. 2013)
62. Define the following terms
 i) Nucleotide
 ii) Anomers
 (iii) Essential amino acids / (A.I.S.B. 2014)
63. (a) Which one of the following is a polysaccharide
 Starch, Maltose, Fructose, Glucose
 (b) What is the difference between native protein and denatured protein?
 (c) Write the name of the vitamin responsible for the coagulation of blood. (A.I.S.B. 2015)
64. (i) Write one reaction of D-glucose which cannot be explained by its open chain structure.

- (ii) What type of linkage is present in nucleic acids?
 (iii) Give one example each for water-soluble vitamins and fat-soluble vitamins. (A.I.S.B. 2019)

65. (a) Write the product when D-glucose reacts with conc. HNO_3
 (b) Amino acids show amphoteric behaviour. Why?
 (c) Write one difference between α -helix and β -pleated structures of proteins. (A.I.S.B. 2018)
66. Define the following with an example of each
 (a) Polysaccharides
 b) Denatured protein
 (c) Essential amino acids / (A.I.S.B. 2018)

Long Answer Questions (Carrying 5 marks)

1. (a) State the constitutional differences between DNA and RNA. Write down the names of the bases produced as hydrolysis of DNA.
 b) Draw simple Fischer projections of D-glucose and L-glucose. Can these be labelled enantiomers? (D.S.B. 2005)
2. (a) Write reactions to show how glucose separately reacts with
 i) NH_2OH
 ii) HNiCl_2
 (b) ammoniacal AgNO_3
 b) What do you understand by
 (i) denaturation and
 (ii) renaturation of proteins?
 c) Name the deficiency diseases resulting from lack of vitamins A and E in the diet. (D.S.B. 2005)
3. (a) Name the three major classes of carbohydrates and give an example of each of these classes.
 b) Answer the following
 (i) What type of linkage is responsible for the primary structure of proteins?
 (ii) Name the location where protein synthesis occurs in our body.
 c) Explain the following terms
 (i) Mutarotation
 (ii) Avitaminosis (D.S.B. 2007)

CBSE QUESTIONS

4. (a) Answer the following questions briefly
 (i) What are reducing sugars?
 (ii) What is meant by denaturation of a protein?
 (iii) How is oxygen replenished in our atmosphere?
 b) Define enzymes. (D.S.B. 2007)
- (a) Answer the following questions briefly
 (i) What are two good sources of vitamin A?
 (ii) What are nucleotides?
 (iii) Give an example of simple lipids.
 b) How are carbohydrates classified? (A.I.S.B. 2007)



Hints & Answers

for Revision Exercises

Very Short Answer Questions

3. Hydrogen bonding between NH and $\text{—}\overset{\text{O}}{\parallel}\text{—}\text{C—}$ groups of peptide bonds.
4. Streptokinase
5. tyrosinase, phenylalanine hydroxylase
7. i. Vitamin A ii. Vitamin K
11. Deoxyribose
12. Ribose
13. Cyanocobalamin
14. Ascorbic acid scurvy
15. Thiamine, beriberi
16. Retinol night blindness
18. Zymase

21. Amylose
22. Amylopectin
23. Adenine Guanine
24. Glycine
25. Vitamin D
26. Saccharic acid
30. Peptide linkage
31. Glucose and galactose
32. Glucose and fructose
38. Glucose
34. c 35. b 36. a 37. a 38. a 39. a
40. c) 41. (c. 42. c) 43. a) 44. b 45. c
46. a 47. c 48. d 49. d 50. c 51. d
52. a, 53. (b)

Competition File

Additional Useful Information and Objective Questions

ADDITIONAL USEFUL INFORMATION

► LIPIDS

These are oily, fatty or waxy substances present in living organisms. They constitute those structural components of plants and tissues that are soluble in organic solvents such as chloroform, ether etc. and are sparingly soluble in water. Their main functions are to form part of the structure of biological membranes and to store energy for the cell.

Chemically, **lipids are esters of long chain fatty acids and alcohols**. They can be divided into three main classes:

Simple lipids which constitute long chain fatty acids and their acid derivatives

- i. Compound lipids which give fatty acids, alcohols and other compounds on hydrolysis
- ii) Derived lipids

Simple lipids Oils and fats are simple lipids. These are most abundant lipids. These are esters of glycerol and three fatty acids. These are also called triglycerides. The three fatty acids may be identical or different. The naturally occurring fatty acids may be saturated or unsaturated. For example,

Saturated fatty acids

Lauroic acid $\text{C}_{12}\text{H}_{24}\text{O}_2$ $\text{CH}_3(\text{CH}_2)_{10}\text{COOH}$

Palmitic acid $\text{C}_{16}\text{H}_{32}\text{O}_2$ $\text{CH}_3(\text{CH}_2)_{14}\text{COOH}$

Myristic acid

Stearic acid

$\text{CH}_3(\text{CH}_2)_{12}\text{COOH}$

$\text{CH}_3(\text{CH}_2)_{16}\text{COOH}$

Unsaturated fatty acids contain one or more double bonds;

Elaidic acid $\text{C}_{18}\text{H}_{34}\text{O}_2$ $\text{C}_{18}\text{H}_{34}\text{O}_2$

Linoleic acid

$\text{C}_{18}\text{H}_{32}\text{O}_2$ $\text{C}_{18}\text{H}_{32}\text{O}_2$

$\text{CH}_3(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_7\text{COOH}$

$\text{CH}_3(\text{CH}_2)_4\text{CH}=\text{CHCH}_2\text{CH}=\text{CH}(\text{CH}_2)_5\text{COOH}$

One double bond

Two double bonds

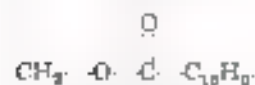
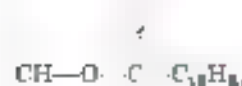
Linolenic acid $\text{C}_{18}\text{H}_{32}\text{O}_2$ $\text{C}_{18}\text{H}_{32}\text{O}_2$

$\text{CH}_3(\text{CH}_2)_3\text{CH}=\text{CHCH}_2\text{CH}=\text{CHCH}_2\text{CH}=\text{CH}(\text{CH}_2)_5\text{COOH}$

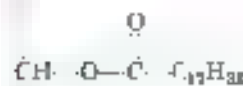
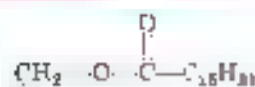
Three double bonds

Oils and fats being glyceryl esters of fatty acids are also called **triglycerides**. The common examples of glycerides are

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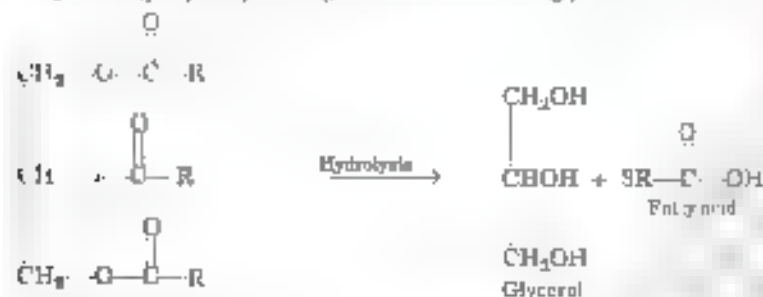
Tripalmitin
a simple glyceride



Palmito-oleo-stearate
a mixed glyceride

The glycerides containing large proportion of saturated acids are solids at room temperature and are called **fats**. On the other hand, the glycerides containing large proportion of unsaturated acids are **liquids** at room temperature and are called **oils**. The oils can be converted into fats by hydrogenation.

They undergo hydrolysis to give one molecule of glycerol and three molecules of fatty acids per molecule of oil or fat.



Triglyceride (oil or fat)

Triglycerides are very important and find uses in soaps, paints, varnishes, printing ink, ointments and creams.

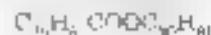
Fatty acids are major sources of energy of the cell. Certain fatty acids like linoleic acid and linolenic acid help the body to synthesise a very important group of compounds called *prostaglandins*. These control almost all physiological activities of the body.

Waxes are also esters and they are simple oils. They are fatty acid esters of long chain monohydric alcohols and may be represented by the general formula $\text{R}^1\text{O}^2\text{R}^3$ where R^1 and R^3 are long hydrocarbon chains. For example,



in bees wax

myrcyl palmitate



in Carnauba wax

myrcyl acetate



in spermaceti

cetyl palmitate

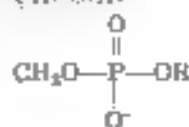
In fact, they occur as mixtures. The waxes are widely spread in nature and play an important role as a protective coatings on fruits, leaves and animals. They have the properties of water insolubility, flexibility and non-reactivity and, therefore, they act as excellent coatings.

Uses: Waxes are used

- in cosmetics, ointments, and as polishes for floors, furniture etc.
- as thin coatings on fruits, leaves, skin and protect the surface from loss of water and attack of micro-organisms.
- in making candles.

Compound lipids The compound lipids on hydrolysis give other substances in addition to alcohols and fatty acids. Phospholipids are examples of compound lipids.

Phospholipids are mixed glycerides of higher fatty acids and phosphoric acid in which two OH groups of glycerol are esterified by fatty acids and third by some derivatives of phosphoric acid.



Phospholipid

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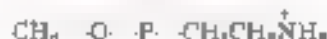
The common examples of phospholipids are **lecithins** and **cephalins** which are found principally in the brain, nerve cells and liver of animals. These are also found in egg yolks, yeast, soyabean and other foods.

Lecithins are derivatives of choline chloride, $\text{HOCH}_2\text{CH}_2\text{N}(\text{CH}_2)_3\text{Cl}^+$

Cephalins are derivatives of ethanolamines, $\text{HOCH}_2\text{CH}_2\text{NH}_2$



O
Lecithin



O
Cephalin

Thus, lecithin contains a quaternary N whereas cephalin contains only primary N.

The phospholipids are good neutral surfactants. They have excellent emulsifying and membrane forming properties. In mayonnaise, the phosphoglycerides of egg yolk keep the oil emulsified in the vinegar.

Derived lipids. Steroids like cholesterol, fat soluble vitamins like vitamins A, D, E and K are the examples of derived lipids.

CELLULAR MEMBRANES

Cellular membranes are constituted mainly of phospholipids and cholesterol. Their relative proportions vary in different cells. The phospholipids are arranged in a double layer (bilayer) with their **hydrophilic** polar phosphate group heads pointing outside and **hydrophobic** non-polar fatty acid chains tails into the interior of the membrane. This bilayer arrangement allows the polar head groups (phosphate ester) to interact with aqueous surroundings both inside and outside the cell and non-polar tails to be away from the aqueous medium. The protein components in the membrane are either embedded in the bilayer or attached to the other side of the membrane depending upon their functions.

The membranes have many specific functions in living organisms. Some of these are

- (i) They maintain the shape of the cell.
- (ii) They control the cellular movements by selectively keeping out certain compounds and transporting others.
- (iii) They keep the cell contents in place.
- (iv) They allow cell-to-cell recognition and contain receptors for many hormones.
- (v) They protect the cell from injury.

OBJECTIVE TYPE QUESTIONS

Multiple Choice Questions

M. C. Q.

A TOPICWISE MULTIPLE CHOICE QUESTIONS
with only one correct answer

Carbohydrates

Select the Correct Answer

A1. Glucose and fructose are

- (a) structural isomers (b) functional isomers
(c) anomers (d) geometrical isomers.

A2. Chlorine is

- (a) aldopentose (b) aldohexose
(c) ketopentose (d) ketohexose.

A3. The monomer units of starch are

- (a) α-glucose (b) β-glucose
(c) pyranose (d) pyranose

A4. Which of the following is the sweetest?

- (a) Glucose (b) Fructose
(c) Maltose (d) Sucrose

A5. Maltose is made up of

- (a) α-D-glucose (b) D-fructose
(c) α-D-glucose and β-D-glucose
(d) glucose and fructose.

A6. Invert sugar is a mixture of

- (a) glucose and fructose
(b) glucose and lactose
(c) glucose and lactose
(d) any glucose

A1. (b), A2. (b), A3. (a), A4. (b), A5. (a), A6. (a)

Competition File

- A7.** Glucose on treatment with sodium amalgam gives
 a) n-heptanoic acid (b) sorbitol
 c) gluconic acid (d) gluconic acid
- A8.** Glucose reacts with X number of molecules of phenyl hydrazine to yield osazone. The value of X is
 a) three (b) two
 c) one (d) four
- A9.** Cellulose is not digestible by human beings due to the absence of cellulose hydrolysing enzyme called
 a) urease (b) cellulase
 c) zymase (d) invertase
- A10.** α -D(+)-glucose and β -D(+)-glucose are
 a) enantiomers (b) geometrical isomers
 c) epimers (d) anomers
- A11.** Complete hydrolysis of cellulose gives
 a) L-glucose (b) D-fructose
 c) D-ribose (d) D-glucose
- A12.** Which of the following is not true about glucose ?
 a) It is an aldohexose
 b) On heating with HI it forms n-hexane
 c) It does not give 2, 4-DNP test
 d) It is present in furanose form
-
- Amino Acids and Proteins**
- A13.** The amino acids are the end products of the digestion of
 a) fats (b) lipids
 c) proteins (d) enzymes
- A14.** The sequence in which amino acids are arranged in a protein is called
 a) primary structure (b) secondary structure
 c) tertiary structure (d) tetrahedral structure
- A15.** The bond that determines the secondary structure of protein is
 a) Covalent bond
 b) Sulphur linkage
 c) Hydrogen bond
 d) Ionic bond
- A16.** Which of the following is a protein ?
 a) Myogen (b) Amylopectin
 c) Keratin (d) Lecithin
- A17.** Which amino acid has no asymmetric carbon atom ?
 a) Histidine (b) Glycine
 c) α -Alanine (d) Threonine
- A18.** Which statement is incorrect about peptide bond ?
 a) C-N bond length in proteins is larger than usual bond length of C-N bond
 b) Spectroscopic analysis shows planar structure of CO-NH group
 c) C-N bond length in proteins is smaller than usual bond length of C-N bond
 d) None of the above
- A19.** In basic medium, alanine exists as
 a) $\text{CH}_3\text{CH}(\text{NH}_3^+)\text{COOH}$ (b) $\text{CH}_3\text{CH}(\text{NH})\text{COOH}$
 c) $\text{CH}_3\text{CH}(\text{NH}_3^+)\text{COO}^-$ (d) $\text{CH}_3\text{CH}(\text{NH})\text{COO}^-$
- A20.** Which of the following is not an essential amino acid ?
 a) Lysine (b) Glycine
 c) Phenylalanine (d) Valine
- A21.** Denaturation of protein leads to loss of its biological activity by
 a) loss of primary structure
 b) loss of primary and secondary structure
 c) loss of secondary and tertiary structure
 d) formation of amino acids
- A22.** In which of the following pair both the proteins are same type (fibrous or globular) ?
 a) myosin, albumin
 b) insulin, collagen
 c) keratin, fibroin
 d) albumin, myosin
-
- Enzymes, Vitamins and Hormones**
- A23.** The chemical messengers produced in ductless glands are called
 a) Lipids (b) Cellular membrane
 c) Hormones (d) Antibodies
- A24.** The hormone which is secreted in the pancreas and controls the metabolism of glucose in the body is
 a) thyroxine (b) oxytocin
 c) insulin (d) cortisone
- A25.** Deficiency of vitamin D leads to disease
 a) Rickets (b) Beri-beri
 c) Scurvy (d) Night-blindness
- A26.** Night-blindness may be caused by the deficiency of vitamin
 a) A (b) B
 c) C (d) D

Competition File

A27. Vitamin A is called

- a. Ascorbic acid b. Retinol
c. Calciferol d. None of these

A28. The only vitamin with metal atom in it is

- a. Vitamin A b. Vitamin K
c. Vitamin B₁₂ d. Vitamin E

A29. Enzymes are regarded as

- a. biocatalysts b. activators
c. messengers d. antibodies.

A30. Which of the following B-group vitamin can be stored in our body

- a. Vitamin B₁ b. Vitamin B₂
c. Vitamin B₆ d. Vitamin B₁₂

A31. Which of the following hormones is an amino acid derivative?

- a. Oxytocin b. Estrone
c. Adrenaline d. Vasopressin

A32. Most appropriate source of vitamin C is

- a. cereals b. egg yolk
c. citrus fruits d. milk

Nucleic acids

A33. Nucleic acids are polymers of

- a. nucleosides b. globulins
c. nucleons d. nucleotides.

A34. The three dimensional structure of DNA was elucidated by

- a. James Watson b. M. Wilkins
c. Deason d. Franklin

A35. Which of the following is not present in DNA?

- a) Adenine b. Guanine
c) Uracil d) Thymine

A36. The chemical change in DNA molecule that could lead to synthesis of proteins with an altered amino acids sequence is called

- a. Replication b. Lipid formation
c. Cellular membrane d) Mutation

A37. In nucleic acids, the individual nucleotides are linked through

- a. peptide linkage b. phosphate group
c. glycosidic linkage d) hydrogen bonds

A38. The relation between the nucleotide triplets and the amino acids is called

- a. Gene b. Genetic code
c. Replication d. Enzymes

A39. Mutation in DNA occurs due to changes in the sequence of

- a) nitrogenous bases
b. ribose units

c) phosphate units

d) hydrogen bonds.

A40. Metabolic activities of cells are controlled by

- a) proteins b) DNA
c) RNA d) fat

A41. Chargoff's rule states that in an organism

a) amount of adenine (A) is equal to that of thymine (T) and the amount of guanine (G) is equal to that of cytosine (C)

b) Amount of adenine (A) is equal to that of guanine (G) and the amount of thymine (T) is equal to that of cytosine (C)

c) Amount of adenine (A) is equal to that of cytosine (C) and the amount of thymine (T) is equal to that of guanine (G).

d) Amount of all bases are equal

A42. Which of the following statement is not correct?

a) Cytosine and thymine are pyrimidines

b) DNA differs from RNA in sugar as well as nitrogenous base

c) In RNA heterocyclic amine base is bonded to C-1' of sugar and the phosphoric acid is bonded to C-5' sugar position

d) In double helix structure of DNA, thymine can bond to cytosine by two hydrogen bonds

A43. In a polynucleotide, the bond which joins two nucleotides is called

a) glycosidic bond b) amine-ester bond

c) phosphoester bond, d) disulphide linkage

A44. Biotin is chemical name of vitamin

a) B₈ b) B

c) H d) K

A45. In double helical structure of DNA, the number of hydrogen bonds involved in thymine and adenine is

a) 1 b) 2

c) 3 d) 9

A46. Which of the following gives maximum energy in metabolic processes?

a) Proteins b) Vitamins

c) Lipids d) Carbohydrates.

A47. Phospholipids are esters of glycerol with

a) three carboxylic acid residues

b) two carboxylic acid residues and one phosphate group

c) one carboxylic acid residue and two phosphate groups

d) three phosphate groups

- A27. b A28. c A29. a A30. d A31. c A32. c A33. d A34. a A35. c A36. d
A37. b A38. b A39. a A40. b A41. a A42. d A43. c A44. c A45. b A46. c
A47. b

Competition File

B (MULTIPLE CHOICE QUESTIONS from Competitive Examinations

AIPMT & Other State Boards' Medical Entrance

B1. Which functional group precipitates in disulphide bond formation in proteins ?

- (a) Thioester (b) Thioether
(c) Thiol (d) Thiolactone

(C.B.S.E. Med. 2005)

B2. Which of the following is a peptide hormone ?

- (a) Testosterone (b) Thyroxine
(c) Adrenaline (d) Insulin

(C.B.S.E. Med. 2005)

B3. The human body does not produce

- (a) vitamins (b) hormones
(c) enzymes (d) DNA (C.B.S.E. Med. 2005)

B4. RNA and DNA are chiral molecules, their chirality is due to

- (a) chiral bases
(b) chiral phosphate ester units
(c) D-sugar component

- (d) L-sugar component (C.B.S.E. Med. 2007)

B5. Which one of the following is an amine hormone ?

- (a) Oxytocin (b) Insulin
(c) Progesterone (d) Thyroxine

(C.B.S.E. PMT 2008)

B6. In DNA, the complementary bases are

- (a) adenine and thymine, guanine and cytosine
(b) adenine and thymine, guanine and uracil
(c) adenine and guanine, thymine and cytosine
(d) uracil and adenine, cytosine and guanine

(C.B.S.E. PMT 2008)

B7. Which of the following hormones contains iodine ?

- (a) Testosterone (b) Adrenaline
(c) Thyroxine (d) Insulin

(C.B.S.E. PMT 2008)

B8. Which of the following does not exhibit the phenomenon of mutarotation ?

- (a) (+) Maltose (b) (-) Fructose
(c) (+) Sucrose (d) Lactose (CBSE PMT 2010)

B9. Which one of the following statements is not true regarding (+) lactose ?

- (a) On hydrolysis (+) lactase gives equal amount of D+ glucose and D+ galactose
(b) (+) Lactose is a β -glucoside formed by the union of a molecule of D+ glucose and a molecule of D+ galactose

(c) (+) Lactose is a reducing sugar and does not exhibit mutarotation

(d) (+) Lactose, $C_{12}H_{22}O_{11}$ contains 8-OH groups

(AIPMT 2011)

B10. Which one of the following does not exhibit the phenomenon of mutarotation ?

(a) (+) Maltose (b) (-) Fructose

(c) (+) Sucrose (d) Lactose (AIPMT 2011)

B11. Which one of the following sets of monosaccharides forms sucrose ?

(a) α -D-galactopyranose and α -D-glucopyranose

(b) α -D-glucopyranose and β -D-fructofuranose

(c) β -D-glucopyranose and α -D-fructofuranose

(d) α -D-glucopyranose and β -D-fructopyranose

(AIPMT 2012)

B12. Deficiency of vitamin B_1 causes the disease

(a) convulsions (b) beri-beri

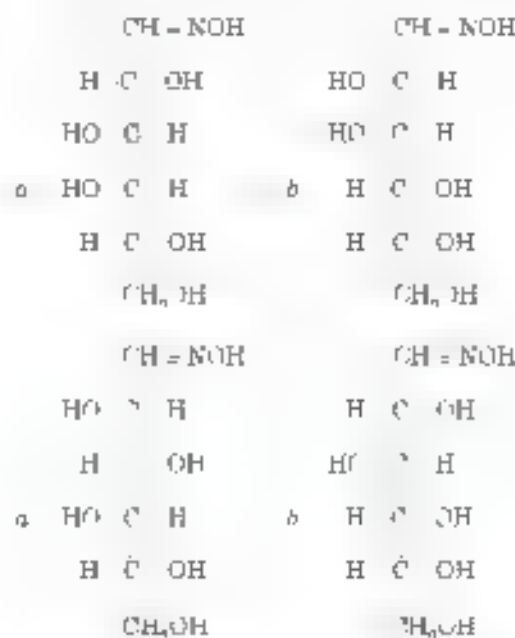
(c) rickets (d) sterility (AIPMT 2012)

B13. Which of the following hormones is produced under the conditions of stress which stimulates glycogenolysis in the liver of human beings ?

(a) Thyroxine (b) Insulin

(c) Adrenaline (d) Estradiol (AIPMT 2014)

B14. D-(-)-glucose reacts with hydroxyl amine and yields an oxime. The structure of the oxime would be



(AIPMT 2014)

- B1. (c) B2. (d) B3. (d) B4. (c) B5. (d) B6. (a) B7. (c) B8. (c) B9. (c) B10. (c)
B11. (b) B12. (b) B13. (c) B14. (d)

Competition File

B15. The correct statement regarding RNA and DNA respectively is

- the sugar component in RNA is α -arabinose and the sugar component in DNA is ribose
- the sugar component in RNA is 2' deoxyribose and the sugar component in DNA is arabinose
- the sugar component in RNA is arabinose and the sugar component in DNA is 2' deoxyribose
- the sugar component in RNA is ribose and the sugar component in DNA is 2' deoxyribose

NEET 2010,

B16. In a protein molecule various amino acids are linked together by

- peptide bond
- alkene bond
- α -glycosidic bond
- β -glycosidic bond

NEET 2010,

B17. Which one given below is a non-reducing sugar?

- Glucose
- Sucrose
- Maltose
- Lactose

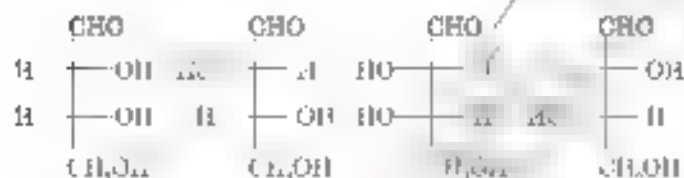
(NEET 2018,

B18. The central dogma of molecular genetics states that the genetic information flows from

- Amino acids \rightarrow Proteins \rightarrow DNA
- DNA \rightarrow Carbohydrates \rightarrow Proteins
- DNA \rightarrow RNA \rightarrow Proteins
- DNA \rightarrow RNA \rightarrow Carbohydrates

(NEET 2010,

B19. The correct corresponding order of names of four aldooses with configuration given below



respectively is

- L-erythrulose, L-threulose, L-erythrulose, D-threulose
- D-threulose, D-erythrulose, L-threulose, L-erythrulose
- L-erythrulose, L-threulose, D-erythrulose, D-threulose
- D-erythrulose, L-threulose, L-erythrulose, L-threulose

NEET 2010,

B20. Which of the following statements is not correct?

- Ovalbumin is a simple food reserve in egg-white.
- Blood proteins thrombin and fibrinogen are involved in blood clotting.

c) Denaturation makes the proteins more active

d) Insulin maintains sugar level in the blood of a human body

(NEET 2017,

B21. The difference between amylose and amylopectin is

- amylopectin have 1 \rightarrow 4 α -linkage and 1 \rightarrow 6 α -linkage
- amylose have 1 \rightarrow 4 α -linkage and 1 \rightarrow 6 β -linkage
- amylopectin have 1 \rightarrow 4 α -linkage and 1 \rightarrow 6 β -linkage
- amylose is made up of glucose and galactose

NEET 2018,

B22. If one strand of DNA has the sequence ATGCTTCA, the sequence in the complementary strand would be

- TCCGAAC
- TACGTA
- TACGAAC
- TAGCTAG

(Kerala P M T 2008,

B23. In aqueous solution, an amino acid exists as

- cation
- anion
- dianion
- zwitter ion

(Kerala PMT 2010)

B24. The linkage between the two monosaccharide units in lactose is

- C₁ of β -D-glucose and C₄ of β -D-galactose
- C₁ of β -D-galactose and C₄ of β -D-glucose
- C₁ of α -D-galactose and C₄ of β -D-glucose
- C₁ of β -D-galactose and C₄ of α -D-glucose
- C₁ of α -D-galactose and C₄ of α -D-glucose

Kerala PMT 2011

B25. A basic amino acid among the following is

- glycine
- valine
- proline
- leucine

(Kerala PMT 2013,

B26. Glucose on oxidation with bromine water gives

- gluconic acid
- tartaric acid
- saccharic acid
- mesoxalic acid

(Kerala PMT 2013,

B27. Chelons and digestive disorders are due to the deficiency of

- vitamin A
- thiamine
- riboflavin
- ascorbic acid

(Kerala PMT 2014,

B28. Glucose does not react with

- Hydroxylamine
- Conc. HNO₃
- acetic anhydride
- sodium bisulphite

(Kerala PMT 2015)

B15. (d) B16. (a) B17. (b) B18. (c) B19. (d) B20. (c) B21. (a) B22. (c) B23. (d) B24. (b) B25. (a)
B26. (a) B27. (c) B28. (d)

Competition File

JEE Main & Other State Boards' Engineering Entrance

- B39.** In both DNA and RNA, heterocyclic base and phosphate ester linkages are at
 (a) C_5' and C_3' respectively of the sugar molecule
 (b) C_3' and C_5' respectively of the sugar molecule
 (c) C_1' and C_2' respectively of the sugar molecule
 (d) C_2' and C_1' respectively of the sugar molecule

A.I.E.E.E 2005

- B30.** The secondary structure of a protein refers to
 (a) hydrophobic interaction
 (b) sequence of α -amino acids
 (c) fixed configuration of the polypeptide backbone
 (d) α -helical backbone. (A.I.E.E.E 2007)
- B31.** The two functional groups present in a typical carbohydrate are
 (a) $-OH$ and $-COOH$
 (b) $-CHO$ and $-COOH$
 (c) $>C=O$ and $-OH$
 (d) $-OH$ and $-CHO$ (A.I.E.E.E 2006)

- B32.** Biuret test is not given by
 (a) Urea (b) Proteins
 (c) Carbohydrates (d) Polypeptides (A.I.E.E.E 2010)

- B33.** The presence or absence of hydroxy group on which carbon atom of sugar differentiates RNA and DNA.
 (a) 1st (b) 2nd
 (c) 3rd (d) 4th (A.I.E.E.E 2011)

- B34.** The change in the optical rotation of freshly prepared solution of glucose is known as
 (a) racemisation (b) specific rotation
 (c) mutarotation (d) tautomerism

A.I.E.E.E 2012

- B35.** Which one of the following statements is correct?
 (a) All amino acids are optically active
 (b) All amino acids except glycine are optically active
 (c) All amino acids except glutamic acid are optically active
 (d) All amino acids except lysine are optically active

A.I.E.E.E 2012

- B36.** Which of the following compounds can be detected by Molisch's test?
 (a) Sugars (b) Amines
 (c) Primary alcohols (d) Nitro compounds

A.I.E.E.E 2012

- B37.** Synthesis of each molecule of glucose in photosynthesis involves

- (a) 6 molecules of ATP
 (b) 18 molecules of ATP
 (c) 10 molecules of ATP
 (d) 8 molecules of ATP (JEE Main 2013)

- B38.** Which one of the following base is not present in DNA?

- (a) quonoline (b) adenine
 (c) cytosine (d) thymine

JEE Main 2014

- B39.** Which of the vitamins given below is water soluble?

- (a) Vitamin E (b) Vitamin K
 (c) Vitamin C (d) Vitamin D

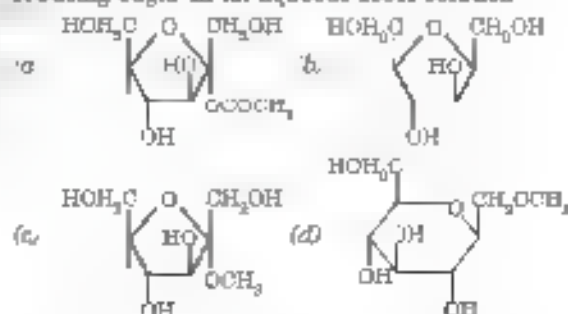
JEE Main 2015

- B40.** Thiol group is present in

- (a) cytosine (b) cystine
 (c) cysteine (d) methionine

JEE Main 2016

- B41.** Which of the following compounds will behave as a reducing sugar in an aqueous KOH solution?



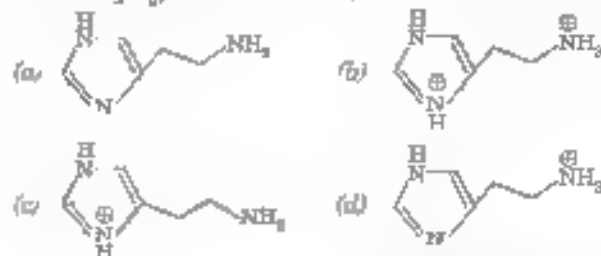
JEE Main 2017

- B42.** Glucose on prolonged heating with HI gives

- (a) *n*-Hexane (b) 1-Hexene
 (c) Hexanoic acid (d) 6-Iodobenzene

JEE Main 2018

- B43.** The predominant form of histamine present in human blood is (pK_a histamine = 6.0)

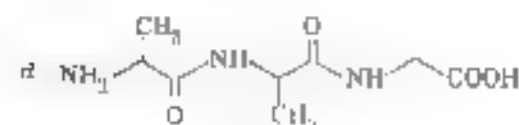
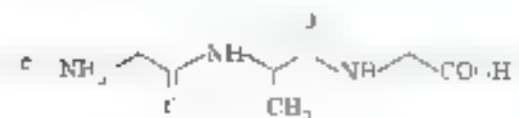
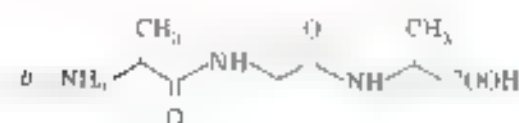
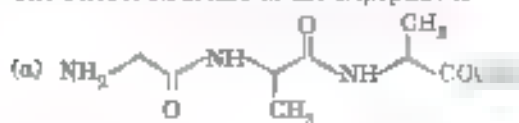


JEE Main 2018

Competition File

B44. A tripeptide is written as Glycine-Alanine-Glycine.

The correct structure of the tripeptide is



Karnataka C E T 2008.

B45. Cellulose is not digestible by human beings due to the absence of a cellulose hydrolysing enzyme called

- (a) cellulase (b) amylase
(c) invertase (d) urease (K.C.E.T 2010)

B46. Lactose is made of

- (a) α -D-glucose only
(b) α -D-glucose and β -D-glucose
(c) α -D-galactose and β -D-glucose
(d) α -D-galactose and α -D-glucose
(e) β -D-galactose and β -D-glucose

Kerala P E T 2010,

B47. α -maltose consists of

- (a) one α -D-glucopyranose unit and one β -D-glucopyranose unit with 1-2 glycosidic linkage
(b) two α -D-glucopyranose units with 1-2 glycosidic linkage
(c) two β -D-glucopyranose units with 1-4 glycosidic linkage
(d) two α -D-glucopyranose units with 1-4 glycosidic linkage

Karnataka C E T 2011

B48. Glucose reacts with Tollen's reagent to give a derivative of

- (a) monocarboxylic acid (b) dicarboxylic acid
(c) ketone (d) keto acid

Orissa JEE 2011.

B49. How many monosaccharides are obtained by hydrolysis of sucrose ?

- (a) 1 (b) 2
(c) 3 (d) 4 (Kerala JEE 2012)

B50. The α - and β -forms of glucose are

- (a) isomers of D- + glucose and L- glucose respectively
(b) diastereomers of glucose
(c) monomers of glucose
(d) isomers which differ in the configuration of C-2
(e) isomers which differ in the configuration of C-5

Kerala P E T 2012.

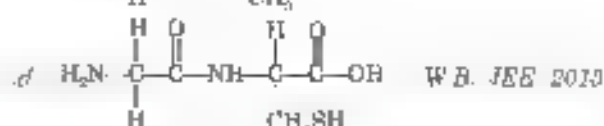
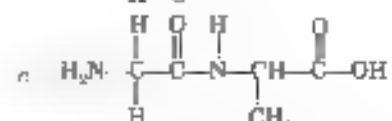
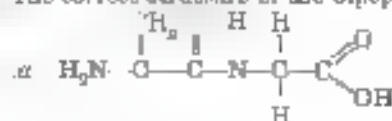
B51. Which one of the following forms the constituent of cell wall of plant cells ?

- (a) Starch (b) Glycogen
(c) Cellulose (d) Amylose
(e) Amylopectin (Kerala P E T 2012)

B52. Sucrose is not a reducing sugar since

- (a) it is chemically stable
(b) it contains no free aldehyde or keto group adjacent to a $>\text{CHOH}$ group
(c) it is built up of a fructose unit
(d) it is optically active (Karnataka C E T 2012)

B53. The correct structure of the dipeptide glyc-alu is



B54. Ribose and 2-deoxyribose can be differentiated by

- (a) Fehling's reagent (b) Tollen's reagent
(c) Barfoed's reagent (d) Osazone formation (W.B. JEE 2013)

B55. Glucose when reduced with H_2 and red phosphorus gives

- (a) n-hexane (b) n-heptane
(c) n-pentane (d) n-octane (Karnataka C E T 2013)

- B44. c B45. a B46. c B47. d B48. a B49. b B50. c B51. c B52. b B53. c B54. d
B55. a

Competition File

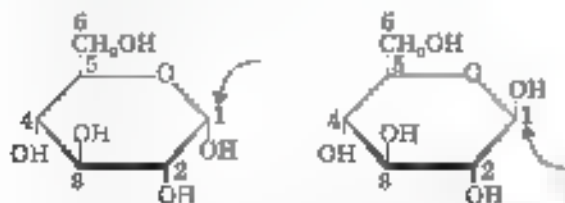
- B56.** How many amino acids are present in insulin ?
 (a) 35 (b) 51
 (c) 20 (d) 22
(Kerala P.E.T. 2013)
- B57.** Which of the following enzymes helps in digestion of proteins?
 (a) Invertase (b) Trypsin
 (c) Tyrosinase (d) Urease *(J.K.C.E.T. 2013)*
- B58.** The statement that is not correct is
 (a) aldose and ketose sugars in alkaline medium do not isomerise
 (b) carbohydrates are optically active
 (c) pentamethate of glucose does not react with hydroxylamine.
 (d) lactose has glycosidic linkage between C_4 of glucose and C_1 of galactose unit. *(Karnataka CET 2014)*
- B59.** Which one of the following is an essential amino acid?
 (a) Cysteine (b) Serine
 (c) Tyrosine (d) Isoleucine
(Karnataka CET 2015)
- B60.** Adenosine is an example of
 (a) purine base (b) nucleoside
 (c) nucleotide (d) pyrimidine base
(Karnataka CET 2015)
- B61.** Glycogen is
 (a) a structural polysaccharide
 (b) structurally similar to amylopectin but extensively branched
 (c) a polymer of β -D- glucose units
 (d) structurally very much similar to amylopectin.
(Karnataka CET 2015)
- B62.** Within the list shown below the correct pair of structures of diamine in pH ranges 2–4 and 9–11 is
 I $H_2N^+ - CH(CH_3)CO_2H$
 II $H_2N - CH(CH_3)CO_2H$
 III $H_3N^+ - CH(CH_3)CO_2^-$
 IV $H_2N - CH(CH_3)CO_2H$
 (a) I, II (b) I, III
 (c) II, III (d) III, IV *(WB JEE 2015)*
- B63.** During conversion of glucose into glucose cyanohydrin, what functional group/atom of glucose is replaced ?
 (a) hydrogen
 (b) aldehydic group
 (c) primary alcoholic group
 (d) secondary alcoholic group *(MH CET 2015)*
- B64.** Which of the following proteins is globular ?
 (a) Collagen (b) Albumin
 (c) Myosin (d) Fibroin *(MH CET 2015)*
- B65.** Glucose on oxidation with bromine water yields gluconic acid. This reaction confirms the presence of
 (a) six carbon atoms linked in straight chain
 (b) secondary alcoholic group in glucose
 (c) aldehyde group in glucose
 (d) primary alcoholic group in glucose
(MH CET 2016)
- B66.** In double strand helix structure of DNA, heterocyclic base cytosine forms hydrogen bond with
 (a) adenine (b) guanine
 (c) purine (d) thymine
 (a) uracil *(Kerala PET 2014)*
- B67.** The amino acid containing mercaptan unit is
 (a) leucine (b) glutamine
 (c) cysteine (d) lysine
 (e) isoleucine *(Kerala PET 2016)*
- B68.** Which one of the following is a non-reducing sugar?
 (a) Maltose (b) Lactose
 (c) Sucrose (d) glucose
 (e) Fructose *(Kerala PET 2016)*
- B69.** Which of the following is correct about H-bonding in DNA?
 (a) A T G C (b) A T T G
 (c) G T A C (d) A A T T
(Karnataka CET 2016)
- B70.** Which of the following gives positive Fehling's solution test?
 (a) Sucrose (b) Glucose
 (c) Pepsin (d) Protein
(Karnataka CET 2016)
- B71.** ADP and ATP differ in the number of
 (a) phosphate units (b) ribose units
 (c) adenine base (d) nitrogen atom
(WB JEE 2017)
- B72.** Hormones are secreted by ductless glands of human body. Iodine containing hormone is
 (a) insulin (b) adrenaline
 (c) testosterone (d) thyroxine
(Karnataka CET 2017)
- B73.** Pick the wrong statement from the following.
 (a) Consumption of citrus fruits and green leafy vegetables in food prevents scurvy
 (b) Deficiency of vitamin B_6 (pyridoxine) results in convulsions
 (c) Sources of vitamin B_1 are yeast, milk, green vegetables and cereals
 (d) Deficiency of vitamin D causes Xerophthalmia
(Karnataka CET 2017)

Competition File

- B74.** The letter 'D' in D-carbohydrates represents
 (a) dextrorotation (b) direct synthesis
 (c) configuration (d) mutarotation
 (e) optical activity
(Karnataka CET 2010, Kerala PET 2017)
- B75.** The glycosidic linkage present in sucrose is between
 (a) C-1 of α -glucose and C-2 of β -fructose
 (b) C-1 of β -galactose and C-4 of α -glucose
 (c) C-1 of α -glucose and C-4 of α -glucose
 (d) C-1 of α -glucose and C-4 of β -fructose
Karnataka CET 2017

- B76.** Which of the following product(s) is/are formed when fructose is treated with Na-Hg in water?
 (a) Sorbitol and Mannitol
 (b) Sorbitol and n-Hexane
 (c) Mannitol and n-Hexane
 (d) Gluconic acid
(J.K. CET 2018)

- B77.** What is the relationship between the given structures look at the arrows?



- α -D-Glucopyranose β -D-Glucopyranose
 (a) Enantiomers (b) Anomers
 (c) Diastereomers (d) Metamers
(J.K. CET 2018)

- B78.** What is the correct explanation of the non-reducing property of sucrose?
 (a) α -D-glucopyranose and β -D-fructofuranose are linked via C₂ and C₁ centres respectively
 (b) α -D-glucopyranose and β -D-fructofuranose are linked via C₁ and C₂ centres respectively
 (c) α -D-glucopyranose and β -D-fructofuranose are linked via C₂ and C₄ centres respectively
 (d) α -D-glucopyranose and β -D-fructofuranose are linked via C₃ and C₄ centres respectively
(J.K. CET 2018)

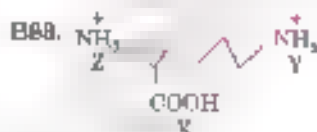
- B79.** What will be the nature of existence of an amino acid containing one amino and one carboxylic acid group in solution of pH < pK_{a1}?
 (a) It exists as anion
 (b) It exists as cation
 (c) It exists as zwitter ion
 (d) It exists as neutral species with no charge
(J.K. CET 2018)

- B80.** The two forms of D-glucopyranose are called
 (a) diastereomers (b) anomers
 (c) epimers (d) enantiomers
Karnataka CET 2018

- B81.** The glycosidic linkage involved in linking the glucose units in amylase part of starch is
 (a) C₁ - C₄ β -linkage (b) C₁ - C₆ α -linkage
 (c) C₁ - C₆ β -linkage (d) C₁ - C₄ α -linkage
Karnataka CET 2018

- B82.** The nitrogenous base present only in RNA is
 (a) guanine (b) adenine
 (c) cytosine (d) uracil
 (e) thymine
(Kerala PET 2018)

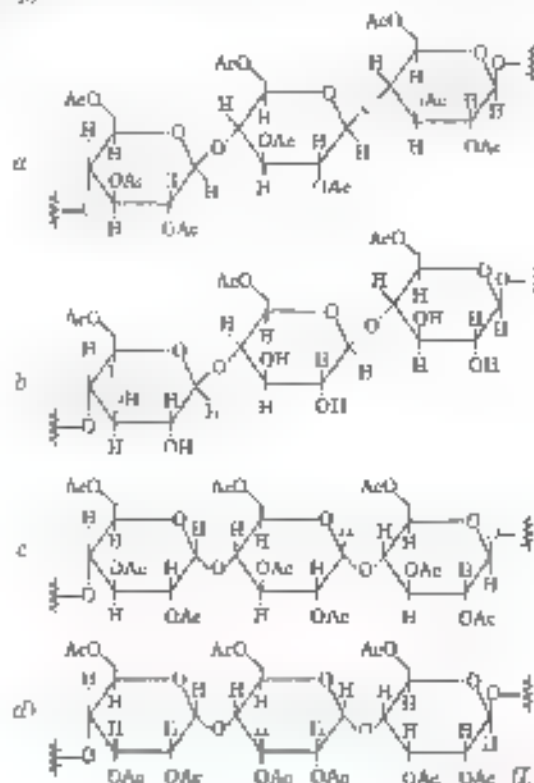
JEE (Advance) for IIT Entrance



Arrange in order of increasing acid strengths

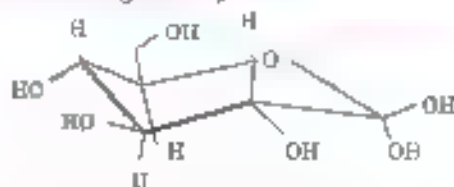
- (a) X > Z > Y (b) Z < X > Y
 (c) X > Y > Z (d) Z > X > Y
(IIT 2004)

- B84.** Cellulose upon acetylation with excess acetic anhydride (CH₃)₂O and pyridine gives cellulose triacetate structure shown as



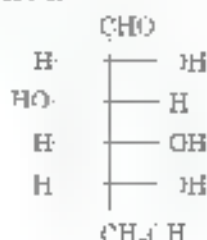
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B85. The following carbohydrate is

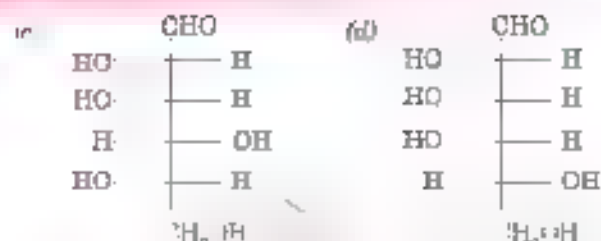
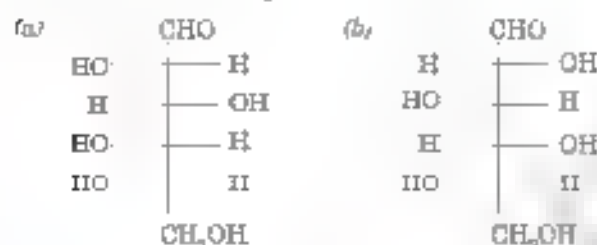


- (a) a ketohexose (b) an aldohexose
(c) an α -furanose (d) an α -pyranose (I.I.T 2011)

B86. The structure of D-(-)-glucose is

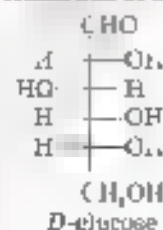


The structure of L-(-)-glucose is

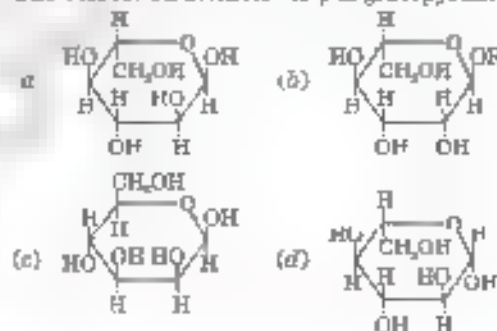


(JEE Advance 2015)

B87. The Fischer presentation of D-glucose is given below



The correct structure(s) of β -D-glucopyranose is/are



(JEE Advance 2018)

B85. (b) B86. (a) B87. (d)

C { MULTIPLE CHOICE QUESTIONS with more than one correct answer

- C1. Carbohydrates which give two molecules of monosaccharides are called disaccharides. These are
(a) maltose (b) cellulose
(c) maltose (d) lactose
- C2. Starch is a mixture of
(a) amylose (b) amylopectin
(c) amylose (d) β -D-glucose
- C3. Which of the following are essential amino acids?
(a) Valine (b) Lysine
(c) Alanine (d) Serine

- C4. Which of the following contain transition metal?
(a) Vitamin B₁₂ (b) Chlorophyll
(c) Hemoglobin (d) DNA
- C5. Which of the following has glycosidic linkage?
(a) Maltose (b) Amylose
(c) Galactose (d) Sucrose
- C6. Fibrous proteins are present in
(a) myosin (b) albumin
(c) collagen (d) fibrin
- C7. The substituted pyrimidines are
(a) adenine (b) uracil
(c) cytosine (d) guanine

C1. (a), (d) C2. (b), (c) C3. (a), (b) C4. (a), (c)

C5. (b), (c)

C6. (a), (b), (d)

C7. (a), (c), (d)

Competition File

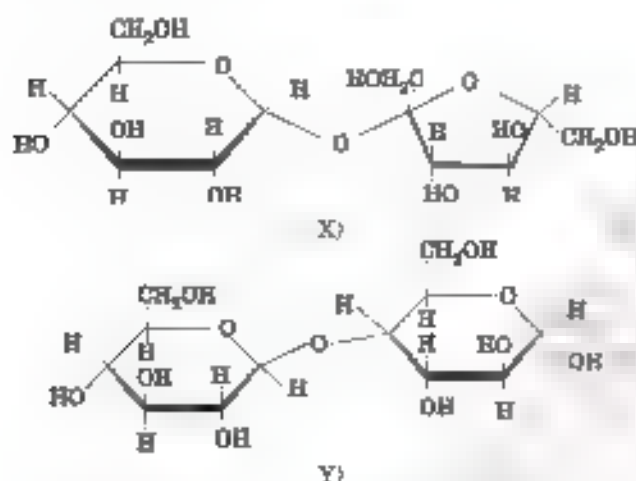
C8. Which of the following statements is/are correct ?

- Adenine and cytosine are substituted purines
- the sugar present in DNA nucleoside is deoxyribose
- RNA contains uracil instead of thymine present in DNA
- In nucleic acids, a phosphate group is bonded to a hydroxyl group of sugar

C9. Which of the following statements is/are not true ?

- Collagen in tendons is a globular protein
- Keratin protein present in hair has α -helix structure
- Coagulation of albumin present in white of an egg is an example of denaturation of protein.
- The enzymes are not specific in nature.

C10. The correct statement(s) about the following sugars X and Y are

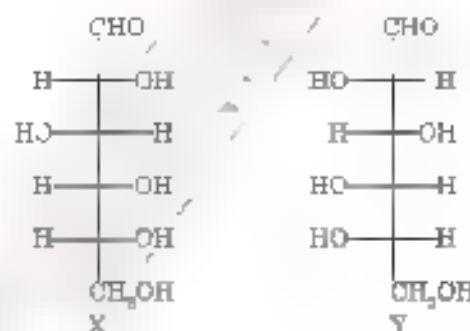


- X is a reducing sugar and Y is a non-reducing sugar
- X is a non-reducing sugar and Y is a reducing sugar

c. The glycosidic linkages in X) and Y) are α and β -respectively

d. The glycosidic linkages in X) and Y) are β and α -respectively JIT-JEE 2009

C11. Among the following statements about the molecules X and Y the one(s) which is (are) correct is (are)



(a) X and Y are diastereomers

b) X and Y are enantiomers

(c) X and Y are both aldohexoses

d) X is a D sugar and Y is an L sugar WB JEE 2014

C12. For 'invert sugar' the correct statement(s) is(are) Given specific rotations of $+$ -sucrose, $+$ -maltose, L- glucose and L-(+)-fructose in aqueous solution are $+66^\circ$, $+113^\circ$, -52° and $+92^\circ$ respectively.

a) 'invert sugar' is prepared by acid catalyzed hydrolysis of maltose

b) 'invert sugar' is an equimolar mixture of D-(+)-glucose and D-(+)-fructose

c) specific rotation of invert sugar is 20°

d) on reaction with Br₂ water 'invert sugar' forms saccharic acid as one of the products. JEE Advance 2010

C8. (b), (c), (d)

C9. (b), (d)

C10. b), (c)

C11. (b), (c), (d)

C12. b), (c)

Passage 1

Monosaccharides are polyhydroxy aldehydes and ketones which cannot be hydrolysed into simpler carbohydrates. The monosaccharides containing $-\text{CHO}$ group are called aldoses while those containing $\text{C}=\text{O}$ group are called ketoses. The aldehyde group is always present at C_1 while keto group is generally present at C_2 . All monosaccharides are oxidised by Tollen's reagent and Fehling solution and are called reducing

sugars. The monosaccharide molecules may be assigned D and L-configurations depending upon whether the configuration of the molecule is related to D- or L-glyceraldehyde. If the $-\text{OH}$ group is attached to the carbon adjacent to the $-\text{CH}_2\text{OH}$ group (last chiral carbon) is on the right hand side, it is assigned D-configuration. The molecule is assigned L-configuration if the $-\text{OH}$ group attached to the carbon adjacent to the $-\text{CH}_2\text{OH}$ group is on the left. The monosaccharides contain

one or more chiral carbon atoms. Pentoses and hexoses have cyclic structures: furanose (five membered) and pyranose (six membered). During cyclisation, C_1 in aldohexoses and C_5 in fructose become chiral and the newly formed $-OH$ group may be either on the left or on the right in Fischer projection formulae. These monosaccharides therefore exist in two stereoisomeric forms called α -anomer and β -anomer while C_1 and C_5 are called glycosidic or anomeric carbon. The bonds joining glycosidic carbon are called glycosidic linkages. D- α -glucose exists in two stereoisomeric forms: α -D-glucose and β -D-glucose. When either of these two forms of glucose i.e., α -D-glucose are dissolved in water and allowed to stand, these get slowly converted into other form and an equilibrium mixture of both is formed. This process is called mutarotation.

D (MULTIPLE CHOICE QUESTIONS

based on the given passage/comprehension

Answer to following questions

- D1. The pair of optical isomers of glucose which differ in the configuration only around C_1 atom are called
 (a) epimers (b) Fischer projections
 (c) anomers (d) mutarotational isomers
- D2. The maximum number of optical isomers of glucose expected are
 (a) 8 (b) 12 (c) 16 (d) 25
- D3. Which of the following statements is not correct?
 (a) Monosaccharides reduce Tollen's reagent.
 (b) On dissolving α -D-glucose in water having specific rotation 11.4° its specific rotation decreases.
 (c) Glucose is aldohexose while fructose is ketohexose.
 (d) In D-glucose, $-OH$ group is present to left at 5th carbon atom.
- D4. Two forms of D-glucopyranose are called
 (a) epimers (b) anomers
 (c) enantiomers (d) diastomers.
- D5. Mutarotation does not occur in
 (a) sucrose (b) α -glucose
 (c) L-glucose (d) none of these
- D6. Which of the following pairs give positive Tollen's test?
 (a) Glucose, sucrose (b) Glucose, fructose
 (c) Hexan-1-ol, neopentanol
 (d) Fructose, sucrose

Passage II.

Proteins are high molecular mass complex biomolecules of amino acids. The important proteins required for our body are enzymes, hormones, antibodies, transport proteins, structural proteins, contractile proteins etc. Except for glycine all α -amino acids have chiral carbon atom and have L-configuration. The amino acids exist as dipolar ion called zwitter ion, in which a proton goes from the carboxyl group to the amino group. A large number of α -amino acids are joined by peptide bonds forming polypeptides. The peptides having very large molecular mass more than 10,000 are called proteins. The structure of proteins is described as primary structure giving sequence of linking of amino acids, secondary structure giving manner in which polypeptide chains are arranged and folded; tertiary structure giving folding, coiling or bending polypeptide chains producing three dimensional structures and quaternary structure giving arrangement of sub-units in an aggregate protein molecule.

Answer the following questions

- D7. Which of the following α -amino acid does not form optical isomers?
 (a) $N^+H_3CH(CH_3)COO^-$
 (b) $N^+H_3CH_2COO^-$
 (c) $N^+H_3CH(CH_2Ph)COO^-$
 (d) $N^+H_3CH(CH_2CH_2)COO^-$
- D8. Which of the following statements is not correct?
 (a) Amino acids exist as zwitter ions.
 (b) All naturally occurring α -amino acids have $-NH_2$ group on the right.
 (c) Except glycine, all other naturally occurring α -amino acids have a chiral carbon atom.
 (d) The basic character in α -amino acids is due to the $-COO^-$ group.
- D9. All proteins on hydrolysis give
 (a) peptides (b) α -amino acids
 (c) amides and carboxylic acid residues
 (d) enzymes
- D10. The sequence in which amino acids are arranged in a protein is called
 (a) primary structure (b) secondary structure
 (c) tertiary structure (d) configuration.
- D11. Which of the following is not a class of proteins?
 (a) enzymes (b) hormones
 (c) antibodies (d) lipids

Passage I: D1. c

D2. c

D3. d

D4. b

D5. a

D6. b

Passage II: D7. b

D8. b

D9. b

D10. a

D11. d

11/7/2004

Competition File

Assertion Reason Type Questions

The questions given below consist of an Assertion and Reason. Use the following key to choose the appropriate answer.

- (a) If both assertion and reason are CORRECT and reason is the CORRECT explanation of the assertion.
- (b) If both assertion and reason are CORRECT but reason is NOT THE CORRECT explanation of the assertion.
- (c) If assertion is CORRECT and reason is INCORRECT.
- (d) If assertion is INCORRECT but reason is CORRECT.
- (e) If both assertion and reason are INCORRECT.

1. **Assertion:** Glycosides are hydrolysed in acidic conditions.

Reason: Glycosides are acetals. *A.I.I.M.S. 2003*

2. **Assertion:** A solution of sucrose in water is dextrorotatory but on hydrolysis in presence of little hydrochloric acid, it becomes levorotatory.

Reason: Sucrose on hydrolysis gives unequal amounts of glucose and fructose as a result of which change in sign of rotation is observed.

3. **Assertion:** Fats and oils are one of the main sources of food for all living organisms.

Reason: Lipids act as energy reserves.

4. **Assertion:** The newly formed RNA dictates the synthesis of protein at the ribosome.

Reason: DNA has a double helical structure while RNA has single stranded structure.

5. **Assertion:** Uracil is present in DNA.

Reason: DNA undergoes replication.

6. **Assertion:** Cellulose is not digested by human beings.

Reason: Cellulose is a polymer of β -D-glucose.

7. **Assertion:** Vitamin A and D are not absorbed in the body unless its digestion and absorption proceed normally.

Reason: Vitamin A and D are fat soluble vitamins.

8. **Assertion:** Except glycine all naturally occurring α -amino acids are optically active.

Reason: All α -amino acids occurring naturally except glycine has at least one asymmetric carbon.

9. **Assertion:** Insulin is a globular protein.

Reason: Globular proteins are water soluble.

10. **Assertion:** Fructose does not contain an aldehyde group but still reduces Tollens reagent.

Reason: In the presence of a base, fructose undergoes rearrangement to form glucose and mannose.

1. (a) 2. (c) 3. (a) 4. (b) 5. (d) 6. (b) 7. (a) 8. (a) 9. (a) 10. (a)

Matrix Match Type Question

Each question contains statements given in two columns, which have to be matched. Statements in Column I are labelled as A, B, C and D whereas statements in Column II are labelled as p, q, r and s. Match the entries of Column I with appropriate entries of Column II. Each entry in Column I may have one or more than one correct option from Column II. The answers to these questions have to be appropriately bubbled as illustrated in the following example.

If the correct matches are A-q, A-r, B-p, B-r, C-r, C-s and D-q, then the correctly bubbled matrix will look like the following.

	p	q	r	s
A	<input checked="" type="radio"/>	<input checked="" type="radio"/>	<input type="radio"/>	<input type="radio"/>
B	<input type="radio"/>	<input type="radio"/>	<input checked="" type="radio"/>	<input checked="" type="radio"/>
C	<input type="radio"/>	<input type="radio"/>	<input checked="" type="radio"/>	<input type="radio"/>
D	<input type="radio"/>	<input checked="" type="radio"/>	<input type="radio"/>	<input type="radio"/>

1. Match the carbohydrate in Column I with its characteristic given in Column II.

Column I	Column II
A) Lactose	(p) Ketohexose
B) Starch	(q) Disaccharide
C) Sucrose	(r) Polysaccharide
D) Fructose	(s) on hydrolysis gives β -D-glucose and β -D-galactose

2. Match the carbohydrate in Column I with its characteristic given in Column II.

Column I	Column II
A) Keratin	(p) protein
B) Haemoglobin	(q) β -pleated protein
(C) Riboflavin	(r) α -amino acid
D) Glycine	(s) Water soluble vitamin

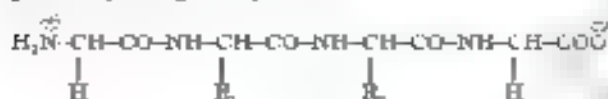
- (1) A - q, s B - r, s C - q, r D - p 2. A - p, q B - p C - r D - s

Competition File

Integer Type Questions

Integer Type: The answer to each of the following question is a **single-digit** integer ranging from 0 to 9.

- Among the following total number of essential amino acids: Leucine, Alanine, Phenylalanine, Proline, Threonine, Lysine, Histidine, Arginine, Cysteine, Tryptophan, Serine, Valine is _____.
- The number of tripeptides formed by three amino acids glycine, alanine and serine is _____.
- The number of chiral carbon atoms present in β -D(+)-glucose is _____.
- The number of peptide hormones among insulin, testosterone, oxytocin, thyroxine, vasopressin, cortisone is _____.
- The number of fat-soluble vitamins among, D, K, B₁₂, C, B₂, E is _____.
- The substituents R₁ and R₂ for nine peptides are listed in the table given below. How many of these peptides are positively charged at pH = 7.4?



Peptide	R ₁	R ₂
I	H	H
II	H	CH ₃
III	CH ₃ COOH	H
IV	CH ₃ CONH ₂	CH ₃ CH ₂ NH ₂
V	CH ₃ CH ₂ NH ₂	CH ₃ CH ₂ CONH ₂
VI	CH ₃ CH ₂ CH ₂ NH ₂	CH ₃ CH ₂ CH ₂ CH ₂ NH ₂
VII	CH ₃ CH ₂ OH	CH ₃ CONH ₂
VIII	CH ₃ H	CH ₃ CH ₂ CH ₂ NH ₂
IX	CH ₃ CH ₂ NH ₂	CH ₃

(IIT JEE 2012)

- When the following aldohexose exists in its D-configuration, the total number of stereoisomers in its pyranose form is _____.



(IIT JEE 2012)

- A tetrapeptide has COOH group on alanine. This produces glycine (Gly), valine (Val), phenyl-alanine (Phe) and alanine (Ala), on complete hydrolysis. For this tetrapeptide, the number of possible sequences (primary structures) with NH₂ group attached to a chiral center is _____.

(JEE Advance 2013)

1. 8

2. 6

3. 7

4. 3

5. 3

6. 4

7. 8

8. 4



NCERT

Exemplar Problems

Objective Questions

- (a) Amylose (b) Amylopectin
(c) Cellulose (d) Glucose

- Which of the following polymer is stored in the liver of animals?

- (a) Amylose (b) Cellulose
(c) Amylopectin (d) Glycogen

Multiple Choice Questions (Type-I)

- Glycogen is a branched chain polymer of α -D-glucose units in which chain is formed by C₁–C₄ glycosidic linkage whereas branching occurs by the formation of C₁–C₆ glycosidic linkage. Structure of glycogen is similar to _____.

1. (b)

2. (d)

Competition File

3. Sucrose (cane sugar) is a disaccharide. One molecule of sucrose on hydrolysis gives

- 2 molecules of glucose
- 2 molecules of glucose + 1 molecule of fructose
- 1 molecule of glucose + 1 molecule of fructose
- 2 molecules of fructose

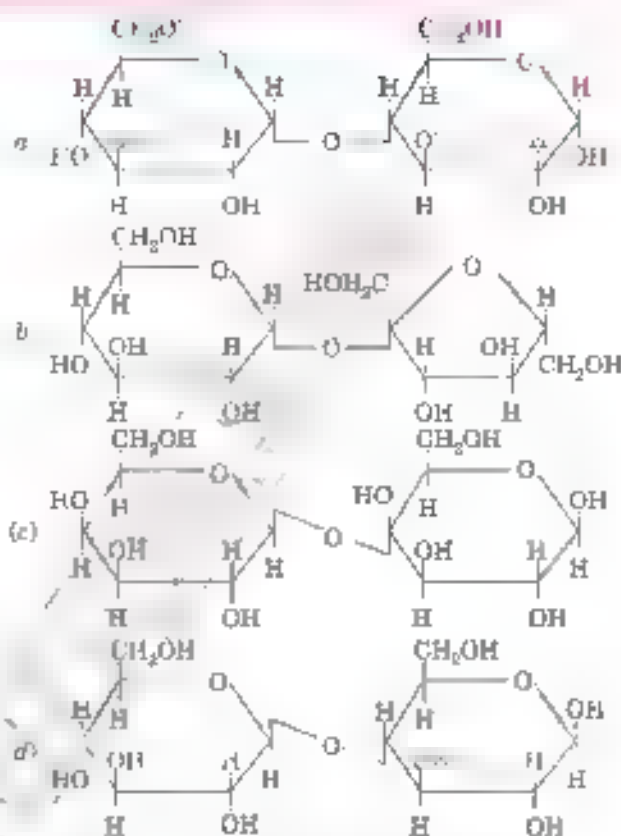
4. Which of the following pairs represents enomers?

	$\begin{array}{c} \text{CHO} \\ \\ \text{H} - \text{C} - \text{OH} \\ \\ \text{HO} - \text{C} - \text{H} \\ \\ \text{H} - \text{C} - \text{OH} \\ \\ \text{CH}_2\text{OH} \end{array}$		$\begin{array}{c} \text{CHO} \\ \\ \text{HO} - \text{C} - \text{H} \\ \\ \text{HO} - \text{C} - \text{H} \\ \\ \text{H} - \text{C} - \text{OH} \\ \\ \text{CH}_2\text{OH} \end{array}$
a)			
	$\begin{array}{c} \text{CHO} \\ \\ \text{H} - \text{C} - \text{OH} \\ \\ \text{HO} - \text{C} - \text{H} \\ \\ \text{H} - \text{C} - \text{OH} \\ \\ \text{CH}_2\text{OH} \end{array}$		$\begin{array}{c} \text{CHO} \\ \\ \text{HO} - \text{C} - \text{H} \\ \\ \text{H} - \text{C} - \text{OH} \\ \\ \text{HO} - \text{C} - \text{H} \\ \\ \text{CH}_2\text{OH} \end{array}$
b)			
	$\begin{array}{c} \text{CHO} \\ \\ \text{H} - \text{C} - \text{OH} \\ \\ \text{HO} - \text{C} - \text{H} \\ \\ \text{H} - \text{C} - \text{OH} \\ \\ \text{CH}_2\text{OH} \end{array}$		$\begin{array}{c} \text{CHO} \\ \\ \text{HO} - \text{C} - \text{H} \\ \\ \text{H} - \text{C} - \text{OH} \\ \\ \text{HO} - \text{C} - \text{H} \\ \\ \text{CH}_2\text{OH} \end{array}$
c)			
	$\begin{array}{c} \text{CHO} \\ \\ \text{H} - \text{C} - \text{OH} \\ \\ \text{HO} - \text{C} - \text{H} \\ \\ \text{H} - \text{C} - \text{OH} \\ \\ \text{CH}_2\text{OH} \end{array}$		$\begin{array}{c} \text{CHO} \\ \\ \text{HO} - \text{C} - \text{H} \\ \\ \text{H} - \text{C} - \text{OH} \\ \\ \text{HO} - \text{C} - \text{H} \\ \\ \text{CH}_2\text{OH} \end{array}$
d)			

5. Proteins are found to have two different types of secondary structures viz. α -helix and β -pleated sheet structure. α -helix structure of protein is stabilised by

- Peptide bonds
- van der Waals forces
- Hydrogen bonds
- Dipole-dipole interactions

6. In disaccharides, if the reducing groups of monosaccharides i.e. aldehydic or ketonic groups are bonded, these are non-reducing sugars. Which of the following disaccharide is a non-reducing sugar?



7. Which of the following acids is a vitamin?

- Aspartic acid
- Ascorbic acid
- Adipic acid
- Saccharic acid

8. Dinucleotide is obtained by joining two nucleotides together by phosphodiester linkage. Between which carbon atoms of pentose sugars of nucleotides are these linkages present?

- 5' and 3'
- 1' and 5'
- 5 and 6
- 3' and 5'

9. Nucleic acids are the polymers of

- Nucleosides
- Nucleotides
- Bases
- Sugars

10. Which of the following statements is not true about glucose?

- It is an aldohexose.
- On heating with HI + formic acid, it forms α -hexane.
- It is present in furanose form.
- It does not give 2,4-DNP test.

11. Each polypeptide in a protein has amino acids linked with each other in a specific sequence. This sequence of amino acids is said to be

- primary structure of proteins.
- secondary structure of proteins.
- tertiary structure of proteins.
- quaternary structure of proteins.

Competition File

12. DNA and RNA contain four bases each. Which of the following bases is not present in RNA?

- a) Adenine (b) Uracil
c) Thymine (d) Cytosine

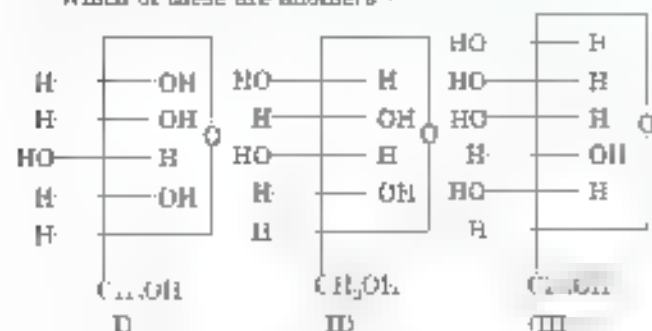
13. Which of the following B group vitamins can be stored in our body?

- a) Vitamin B₁ (b) Vitamin B₂
c) Vitamin B₆ (d) Vitamin B₁₂

14. Which of the following bases is not present in DNA?

- a) Adenine (b) Thymine
c) Cytosine (d) Uracil

15. Three cyclic structures of monosaccharides are given below. Which of these are anomers?

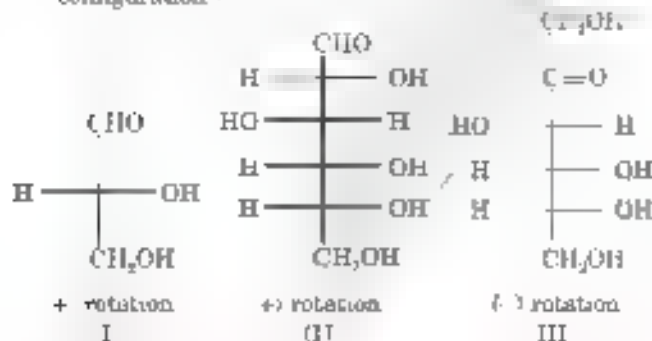


- a) I and II (b) II and III
c) I and III
d) All is anomer of I and II

16. Which of the following reactions of glucose can be explained only by its cyclic structure?

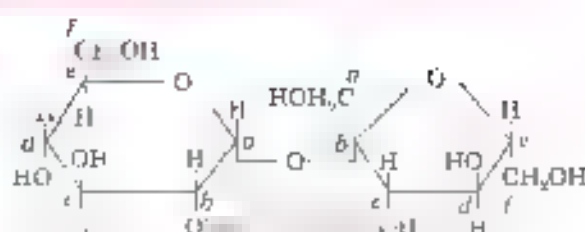
- a) Glucose forms pentacetate
b) Glucose reacts with hydroxylamine to form an oxime.
c) Pentacetate of glucose does not react with hydroxylamine
d) Glucose is oxidised by nitric acid to gluconic acid.

17. Optical rotations of some compounds along with their structures are given below. Which of them have D configuration?



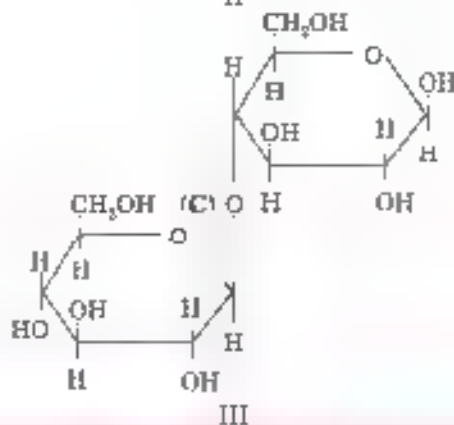
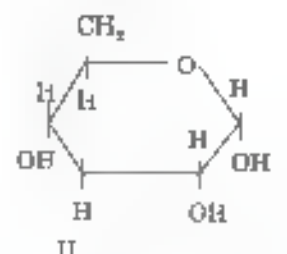
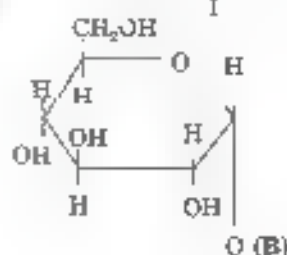
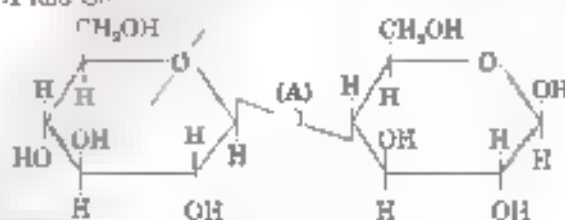
- a) I, II, III (b) II, III
c) I, II (d) III

18. Structure of a disaccharide formed by glucose and fructose is given below. Identify anomeric carbon atoms in monosaccharide units.



- a) a carbon of glucose and a carbon of fructose
b) a carbon of glucose and c carbon of fructose
c) a carbon of glucose and o carbon of fructose
d) f carbon of glucose and f carbon of fructose.

19. Three structures are given below in which two glucose units are linked. Which of these linkages between glucose units are between C1 and C4 and which linkages are between C1 and C6?



Competition File

- a) A is between C1 and C4, B and C are between C1 and C6
 b) A and B are between C1 and C4, C is between C1 and C6
 c) A and C are between C1 and C4, B is between C1 and C6
 d) A and C are between C1 and C6, B is between C1 and C4

Multiple Choice Questions (Type-B)

Note: In the following questions two or more options may be correct.

20. Carbohydrates are classified on the basis of their behaviour on hydrolysis and also as reducing or non-reducing sugar. Sucrose is a
 a) monosaccharide (b) disaccharide
 c) reducing sugar (d) non-reducing sugar
21. Proteins can be classified into two types on the basis of their molecular shape i.e. fibrous proteins and globular proteins. Examples of globular proteins are
 a) Insulin (b) Keratin
 c) Albumin (d) Myosin
22. Which of the following carbohydrates are branched polymer of glucose?
 a) Amylose (b) Amylopectin
 c) Cellulose (d) Glycogen
23. Amino acids are classified as acidic, basic or neutral depending upon the relative number of amino and carboxyl groups in their molecule. Which of the following are acidic?
 a) $(\text{CH}_3)_2\text{CH}-\text{CH}(\text{COOH})-\text{NH}_2$
 b) $\text{HOOC}-\text{CH}_2-\text{CH}_2-\text{CH}(\text{COOH})-\text{NH}_2$
 c) $\text{H}_2\text{N}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{COOH}$
 d) $\text{HOOC}-\text{CH}_2-\text{CH}(\text{COOH})-\text{NH}_2$

24. Lysine, $\text{H}_2\text{N}-(\text{CH}_2)_4-\text{CH}(\text{COOH})-\text{NH}_2$ is

- a) α -Amino acid
 b) Basic amino acid
 c) Amino acid synthesised in body
 d) β -Amino acid

25. Which of the following monosaccharides are present as five membered cyclic structure (furanose structure)?

- a) Ribose (b) Glucose
 c) Fructose (d) Galactose

26. In fibrous proteins, polypeptide chains are held together by
 a) van der Waals forces
 b) disulphide linkage
 c) electrostatic forces of attraction
 d) hydrogen bonds
27. Which of the following are purine bases?
 a) Guanine (b) Adenine
 c) Thymine (d) Uracil
28. Which of the following terms are correct about enzymes?
 a) Proteins (b) Inorganic
 c) Nucleic acids (d) Biocatalysts

Matching Type Questions

Note: Match the items of Column I and Column II in the following questions. More than one option in Column I may match with the items given in Column II.

29. Match the vitamins given in Column I with the deficiency disease they cause given in Column II.

Column I (Vitamins)	Column II (Diseases)
a) Vitamin A	(i) Pernicious anaemia
b) Vitamin B ₁₂	(ii) Increased blood clotting time
c) Vitamin B ₁₀	(iii) Kerophthalmus
d) Vitamin C	(iv) Rickets
e) Vitamin D	(v) Muscular weakness
f) Vitamin E	(vi) Night blindness
g) Vitamin K	(vii) Beri-Beri
	(viii) Bleeding gums
	(ix) Osteomalacia

30. Match the following enzymes given in Column I with the reactions they catalyse given in Column II.

Column I (Enzymes)	Column II (Reactions)
(a) Invertase	(i) Decomposition of urea into NH_3 and CO_2
b) Maltase	(ii) Conversion of glucose into ethyl alcohol
c) Pepsin	(iii) Hydrolysis of maltose into glucose
d) Urease	(iv) Hydrolysis of cane sugar
e) Zymase	(v) Hydrolysis of proteins into peptides

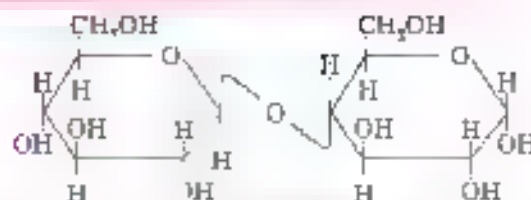
20. (b), (d) 21. a, (c) 22. (b), (d) 23. b, (d) 24. a) (b) 25. (a), (c) 26. (b), (d) 27. a, (b) 28. a, (d)
 29. a - (vii); b - (ix); c - (ii); d - (iv); e - (v); f - (vi); g - (viii)
 30. (a) - (iv); (b) - (iii); (c) - (v); (d) - (i); (e) - (ii)

Competition File

Assertion and Reason Type Questions

Note : In the following questions a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices.

- (a) Assertion and reason both are correct statements and reason explains the assertion.
 (b) Both assertion and reason are wrong statements.
 (c) Assertion is correct statement and reason is wrong statement.
 (d) Assertion is wrong statement and reason is correct statement.
 e Assertion and reason both are correct statements but reason does not explain assertion.
31. **Assertion :** D(+), Glucose is dextrorotatory in nature.
Reason : 'D' represents its dextrorotatory nature.
32. **Assertion :** Vitamin D can be stored in our body.
Reason : Vitamin D is fat soluble vitamin.
33. **Assertion :** β -glycosidic linkage is present in maltose.



Reason : Maltose is composed of two glucose units in which C-1 of one glucose unit is linked to C-4 of another glucose unit.

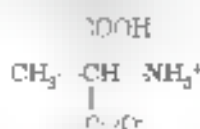
34. **Assertion :** All naturally occurring α -amino acids except glycine are optically active.
Reason : Most naturally occurring amino acids have L-configuration.
35. **Assertion :** Deoxyribose $C_5H_{10}O_4$ is not a carbohydrate.
Reason : Carbohydrates are hydrates of carbon so compounds which follow $C_x(H_2O)_y$ formula are carbohydrates.
36. **Assertion :** Glycine must be taken through diet.
Reason : It is an essential amino acid.
37. **Assertion :** In presence of enzyme substrate molecule can be attacked by the reagent effectively.
Reason : Active sites of enzymes hold the substrate molecule in a suitable position.

31. (c) 32. (a) 33. (d) 34. (e) 35. (b) 36. (b) 37. (c)

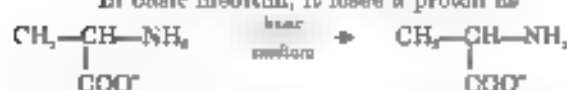
Hints & Explanations for Difficult Objective Type Questions

A. Topicwise multiple choice questions

- A1. (b) Glucose and fructose have same molecular formula $C_6H_{12}O_6$ but have different functional groups, $-CHO$ (glucose) and $>C=O$ (fructose).
- A7. (b)
- $$\begin{array}{c} \text{CHO} \\ | \\ \text{CH(OH)}_4 \\ | \\ \text{CH}_2\text{OH} \end{array} + 2[\text{H}] \xrightarrow{\text{Ni/H}_2} \begin{array}{c} \text{CH}_2\text{OH} \\ | \\ \text{CH(OH)}_4 \\ | \\ \text{CH}_2\text{OH} \end{array}$$
- Sorbitol
- A12. (d) Glucose is present in pyranose form and it is never present in furanose form.
- A19. (c) Alanine is $\text{CH}_3\text{CH}(\text{NH}_2)\text{COOH}$ and exists as Zwitter ion,



In basic medium, it loses a proton as



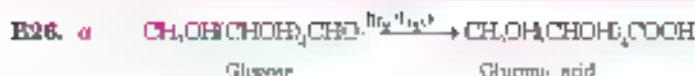
- A21. (e) During denaturation of proteins, secondary and tertiary structures get destroyed but primary structure remains as such.

- A29. (a) Keratin and fibroin are fibrous proteins.
 A30. (d) : Vitamin B_{12} can be stored in our body.
 A42. (d) : Thymine can bond to adenine by 2 hydrogen bonds.
 A44. (c) : Biotin is vitamin H.

B. mcq from Competitive Examinations

- B9. (c) Lactose is a reducing sugar and all reducing sugars show mutarotation.
- B20. (c) Denaturation of proteins loses its biological activity and makes it less active.
- B21. (a) Amylose is a linear polymer of α -D-glucose linked to one another through glycosidic linkages involving C_1 of one glucose and C_4 of next glucose i.e. 1-4 α -linkage. Amylopectin is a branched chain polymer of α -D-glucose units in which chain is formed by C_1 - C_4 α -linkages and branching occurs by C_1 - C_6 α -glycosidic linkages.
- B23. (c) In DNA molecule, only A and T and G and C can combine. A and T are joined by two hydrogen bonds while G and C are joined by three hydrogen bonds.
 So $\text{ATG}^* \text{TTC}^* + \text{TACGAACT}$

Competition File

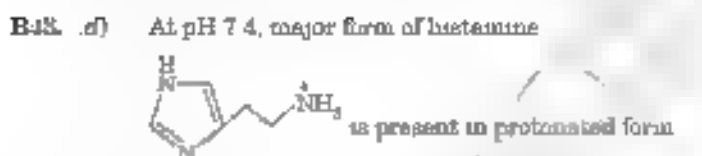
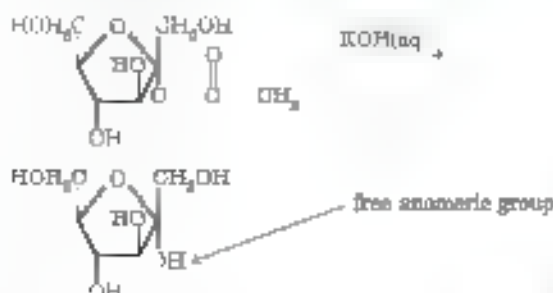


B27. (c) Due to the deficiency of vitamin B₂, riboflavin cheilosis i.e. cracking of lips and corner of the mouth and digestive disorders occur.

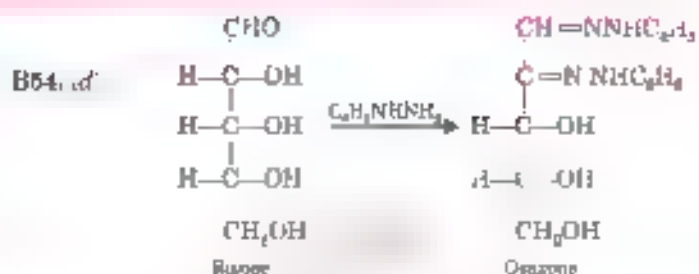
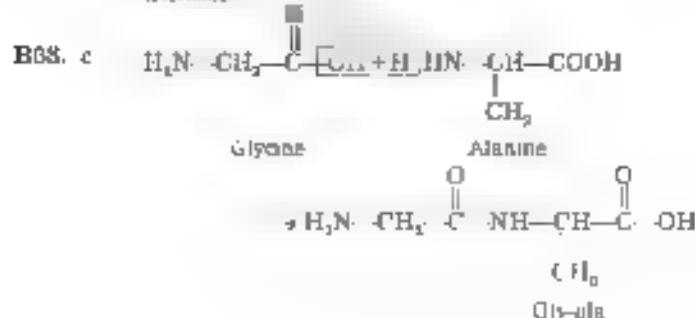
B28. (b) Glycine, $\text{NH}_2\text{CH}_2\text{COOH}$ is optically inactive while all other amino acids are optically active.

B36. (a) Molisch's test is used for the detection of carbohydrates.

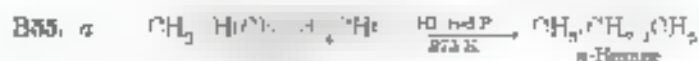
B41. (a) Sugars containing free anomeric -OH group are reducing sugars.



B49. (b) Sucrose is a disaccharide made up of glucose and fructose.



In deoxyribose, one -OH group is missing, which will prevent the formation of osazone.



B56. (b) 51 amino acids are present.

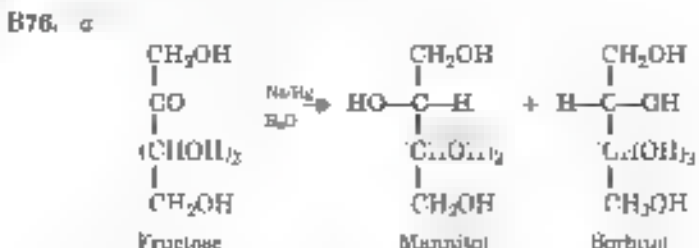
B57. (b) Trypsin catalyzes the hydrolysis of peptide bonds, breaking down proteins into smaller peptides.

B71. (a) ADP is adenosine diphosphate and has two phosphate groups. ATP is adenosine triphosphate and has three phosphate groups. Therefore, ADP and ATP differ in number of phosphate groups.

B73. (d) Deficiency of vitamin A causes Xerophthalmia and deficiency of vitamin D causes rickets.

B74. (c) The letter D in D-carbohydrates represents configuration. A monosaccharide is assigned D-configuration if the -OH group at the last chiral carbon lies towards right hand side.

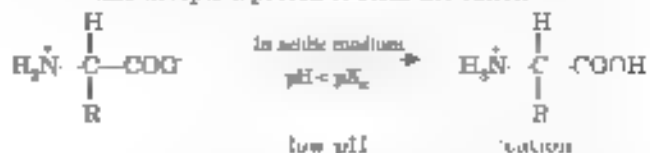
B75. a Glycosidic linkage present in sucrose is between C-1 of α-glucose and C-2 of β-fructose.



B77. b These are isomers which differ in position at C-1 and are called anomers.

B78. (b) Sucrose is a non-reducing sugar because both glucose (C₁-α) and fructose (C₂-β) are connected to each other through their reducing centres.

B79. (b) At low pH acidic solution, COO⁻ acts as a base and accepts a proton to form the cation.

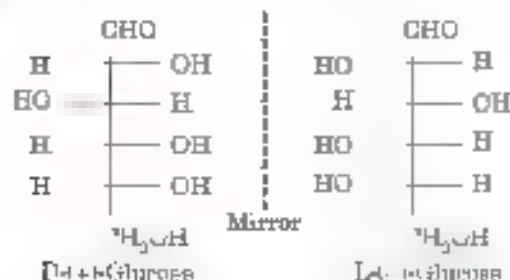


B84. (a) Cellulose has β-glycosidic linkages between C₁ of one glucose unit and C₄ of the other. It has three free OH groups at 2, 3, 6 positions and hence OH group appears at C₂, C₃ and C₆ positions.

Competition File

- B83. b** The carbohydrate has 5 carbon and one oxygen in the ring and hence it has pyranose ring. Further since C_2 -OH is β -oriented, therefore the structure is β -pyranose. The carbohydrate has a total of six carbon atoms and has one -OH and one H at C_4 , therefore, it is aldohexose.

B86. d

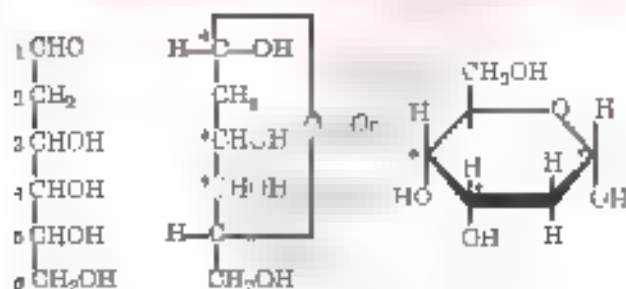


C. mcq with more than one correct answer

- C10. b, c** In sugar (X), reducing ends of both the sugars are not free, hence it is a non-reducing sugar. In sugar (Y), reducing end at C_1 is free, hence it is a reducing sugar.
- C11. (b, c, d)** X and Y are enantiomers and not diastereomers. X and Y are both aldohexoses. But X is a D-sugar and Y is L-sugar.
- C12. b, c** Invert sugar is an equimolar mixture of D-(+)-glucose and D-(-)-fructose. The specific rotation, $[\alpha]$ of L-(-)-glucose and L-(+)-fructose are -52° and $+92^\circ$ respectively. Therefore
 $[\alpha]$ of D-(+)-glucose = $+52^\circ$
 $[\alpha]$ of D-(-)-fructose = -92°
 Specific rotation of invert sugar = $0.5 \times [\alpha]$ of D-(+)-glucose + $0.5 \times [\alpha]$ of D-(-)-fructose
 = $0.5 \times (+52^\circ) + 0.5 \times (-92^\circ) = -20^\circ$

Integer Type Questions

7. 8



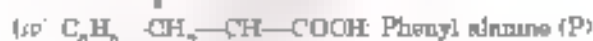
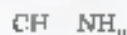
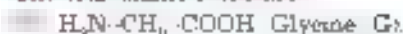
Since the configuration is D, cyclisation will occur at OH of 5th carbon atom.

Chiral centres in pyranose structure, $n = 3$

$$\text{Total stereoisomers} = 2^n = 2^3 = 8$$

B. 4

The four amino acids are



Since A is at the end and G does not contain a chiral centre, then all tetrapeptides begin either with V or P. Thus, different options with NH_2 group attached to a chiral centre are

(i) VPAA (ii) VPGA (iii) PVGA (iv) PGVA

NCERT Exemplar Problems MCQs Type-I

- 2. (d)** Glycogen is stored in the liver of animals.
- 3. c** $\text{C}_{12}\text{H}_{22}\text{O}_{11} + \text{H}_2\text{O} \xrightarrow{\text{H}^+} \text{C}_6\text{H}_{12}\text{O}_6 + \text{C}_6\text{H}_{12}\text{O}_6$
 Sucrose Glucose Fructose
- 4. (c)** Anomers are those cyclic hemiacetals which differ only in the configuration of -OH group at C_1 carbon.
- 6. b)** In option (b) reducing centre of glucose i.e. C_1 is connected to the reducing centre of fructose i.e. C_2 .
- 7. (b)** Ascorbic acid is vitamin C.
- 10. c)** Glucose is never present in furanose form.
- 12. c)** Thymine is not present in RNA.
- 15. a** Structures I and II differ only in the position of -OH group at C_1 and hence are anomers.
- 16. c)** Due to the absence of free OH group at C_2 , cyclic structure of glucose pentaacetate cannot revert to open chain aldehydic form and hence cannot form oxime.
- 17. a** In all the three structures (I, II and III), the configuration of OH at C_1 is towards right and hence all have D-configuration.
- 18. c)** 'a' carbon of glucose and 'b' carbon of fructose.

NCERT Exemplar Problems . MCQs Type-II

- 20. b, d)** Sucrose is a disaccharide and is a non-reducing.
- 22. b, d)** Amylopectin and glycogen both have branched chain structures. These differ only in the number of glucose units in the chain length.
- 24. a, b)** Lysine is a basic amino acid because it has two $-\text{NH}_2$ groups and one $-\text{COOH}$ group. It is not synthesised in the body.
- 26. b, d)** Disulphide linkages and hydrogen bonds.
- 27. a, b)** Adenine and guanine are purine bases.
- 28. a, d)** Enzymes are globular proteins and act as biocatalysts.

Unit Practice Test

for Board Examination

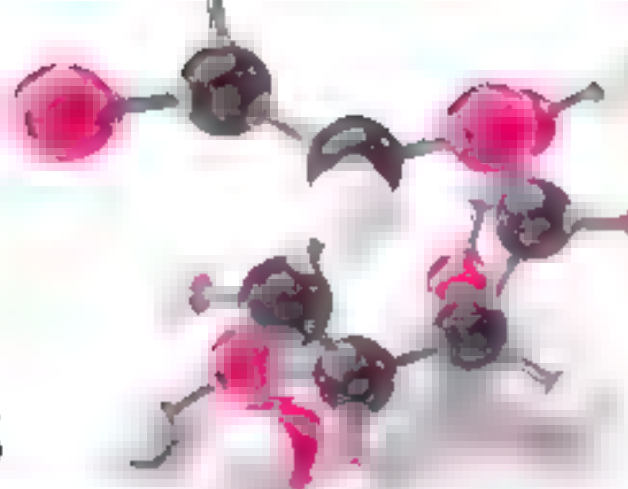
Time allowed : 2 Hrs.

Maximum Marks : 35

1. What are the products of hydrolysis of sucrose ? (1)
2. Which enzyme is used to cure heart disease ? (1)
3. What type of bonds hold a DNA double helix together ? (1)
4. Name the purines present in DNA. (1)
5. Which enzyme is present in saliva ? What is its function ? (1)
6. The two strands in DNA are not identical but are complementary. Explain this statement. (3)
7. Enumerate the reactions of glucose which cannot be explained by its open chain structure. (2)
8. How do you explain the amphoteric character of amino acids. (2)
9. What are the polysaccharides that make up starch and what is the difference between them ? (2)
10. What is glycogen? How is it different from starch? (2)
11. Define the following terms as related to proteins. (3)
 - (i) Primary structure
 - (ii) Peptide linkage
 - (iii) Denaturation.
12. What are essential and non-essential amino acids? Give two examples of each type. Explain the amphoteric behaviour of amino acids. (3)
13. What happens when D-glucose is treated with. (3)
 - (i) Bromine water
 - (ii) Nitric acid
 - (iii) HI
14. (a) What are disaccharides ? Discuss the structure of sucrose. (3)
- (b) What is mutarotation ? (3)
15. Name the products obtained on complete hydrolysis of DNA. Enumerate the differences between DNA and RNA. In what ways a nucleotide is different from nucleoside. Illustrate with examples. (3)
16. (a) What are vitamins ? How are these classified. (2)
- (b) Name the vitamins whose deficiency causes. (3)
 - (i) rickets
 - (ii) beri-beri
 - (iii) night blindness.
- (c) Give two differences between hormones and vitamins. (2)

100

► To check your performance see HINTS AND SOLUTIONS TO SOME QUESTIONS at the end of Part II of the book.



UNIT 15

POLYMERS

By Dr. S. K. Sharma

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With the development of science and technology, man has been trying to prepare new and new compounds to fulfil his needs and make his life comfortable. Polymers are one of the important products of chemical industry which have a great impact on our modern life. With the discovery of polymers, our daily life has become easier and colourful. Plastics, synthetic fibres, synthetic rubber etc. are common examples of polymers. These polymers have multifarious uses ranging from household articles, clothes, furniture, children's toys, packaging bags, automobile tyres, gears and seals, electrical insulating materials, machine parts, etc. to space aircraft and biomedical and surgical operations. Indeed, the polymers are the backbone of four major industries such as plastics, elastomers, fibres, paints and varnishes.

POLYMERS

Polymers are high molecular mass substances consisting of large number of repeating structural units derived from simple molecules.

In Greek, *poly* means many and *mer* means unit or part. They contain macro sized molecules and have very high molecular mass of the order 10^3 – 10^5 u. They are also called **macromolecules**. The repeating structural units are derived from some simple reactive molecules and are linked to each other by covalent bonds.

The simple molecules which combine to give polymers are called **monomers**. The process by which the simple molecules i.e. monomers are converted into polymers is called **polymerisation**. For example, polyethylene or commonly known as *polythene* is a polymer which is obtained from its monomers ethylene by the process of polymerisation.



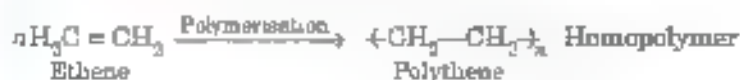
Polymers and macromolecules

The polymers are also called **macromolecules** because of their big size. The terms polymers and macromolecules are often used without any distinction. But, strictly speaking, a polymer always consists of thousands of repeating monomer units. However, a macromolecule is a giant molecule which may or may not contain monomer units. For example, *chlorophyll* is a macromolecule but it is not regarded as a polymer because it does not contain monomers. However, polythene may be regarded as a polymer as well as a macromolecule because it contains a large number of repeating monomers. Thus, **all polymers are macromolecules but all macromolecules are not polymers.**

It may be noted that polymers such as polysaccharides (starch, cellulose), proteins and nucleic acids etc. which control various life processes in plants and animals are also called **biopolymers**.

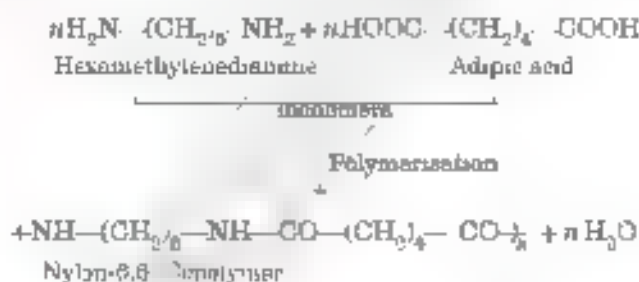
Homopolymer and Co-polymer

A polymer formed from one type of monomers is called **homopolymer**. For example, polythene is a homopolymer of monomer ethene. In this, the repeating structural unit is CH_2-CH_2 .



Some other examples of homopolymers are polypropylene, polyvinyl chloride (PVC), polyisoprene, polyacrylonitrile (PAN), polybutadiene, etc.

A polymer formed from two or more **different monomers** is called **co-polymer or mixed polymer**. For example, nylon-6,6 is a polymer of two types of monomers, hexamethylenediamine and adipic acid.



Other examples of co-polymers are Buna-S, polyesters, bakelite, melamine formaldehyde, etc.

CLASSIFICATION OF POLYMERS

Polymers are classified in a number of ways as described below.

- Classification based on source of availability
- Classification based upon structure.
- Classification based upon molecular forces.
- Classification based upon mode of synthesis.

A. Classification of Polymers on the Basis of Source of Availability

The polymers can be broadly classified as

- Natural polymers.
- Synthetic polymers.
- Semisynthetic polymers.

1. Natural polymers

The polymers obtained from nature (plants and animals) are called **natural polymers**. These occur in plants and animals and are very essential for life. For example, starch, cellulose, natural rubber, proteins, nucleic acids, etc.

2. Synthetic polymers

The polymers which are prepared in the laboratories are called **synthetic polymers**. These are also called **man-made polymers**. For example, polyethylene, PVC, nylon, teflon, bakelite, terylene, synthetic rubber, etc.

These polymers find diverse uses as in clothing, shelter, electric fittings, substitute for wood and metals, household goods, etc.

3. Semisynthetic polymers

These polymers are mostly derived from naturally occurring polymers by chemical modifications. For example, cellulose is a naturally occurring polymer. Cellulose on acetylation with acetic anhydride in the presence of sulphuric

and forms **cellulose diacetate polymer**. It is used in making threads and materials like films, glasses, etc. Other examples of semisynthetic polymers are **carcatted rubber** (used in making tyres etc.) **gun cotton** which is **cellulose nitrate** (used in making explosives, etc).

B. Classification of Polymers on the Basis of Structure

On the basis of structure of polymers, these can be classified as

1. Linear polymers.
2. Branched chain polymers.
3. Cross-linked or network polymers.

1. Linear polymers

These are polymers in which monomeric units are joined together to form long and unbranched chains (Fig. 1a). These linear polymers are well packed and therefore, have high densities, high tensile pulling strength and high melting points. Some common examples of linear polymers are **high density polythene**, **polyvinylchloride (PVC)**, **nylons**, **polyesters**, etc.

2. Branched chain polymers

These are polymers in which the monomers are joined to form long chains with side chains or branches of different lengths (Fig. 1b). These branched chain polymers are irregularly packed and therefore, they have low tensile strength and melting points than linear polymers. Some common examples are

low density polythene, **glycogen**, **starch**, etc.

3. Cross-linked or network polymers

These are polymers in which monomer units are cross-linked together to form a three-dimensional network. These are also called three-dimensional network polymers. These polymers are hard, rigid and brittle because of network structure. These are shown in Fig. 1(c). For example,

bakelite, **melamine formaldehyde resin**, etc.

C. Classification of Polymers on the Basis of Molecular Forces

A large number of applications of polymers depend upon their mechanical properties such as tensile strength, elasticity, toughness, etc. These mechanical properties depend upon intermolecular forces like van der Waals forces, hydrogen bonds and dipole-dipole interactions existing in the macromolecules. Although these intermolecular forces are also present in simple molecules, their effect is less significant in them as compared to macromolecules. This is because in the polymers, these forces extend along the chain resulting significant combined effect. Thus longer the length of the polymer chain, stronger is the effect of intermolecular forces.

Depending upon the intermolecular forces, the polymers have been classified into four types

1. Elastomers.
2. Fibres
3. Thermoplastics.
4. Thermosetting polymers.

1. Elastomers

The polymers in which the intermolecular forces of attraction between the polymer chains are the weakest and have elastic character like rubber* are called **elastomers**. Because of the presence of weak forces, the polymers can be easily stretched by applying small stress and regain their original shape when the stress is removed. The most important example of elastomer is **natural rubber**. These polymers consist of randomly coiled molecular chains of irregular shape having a few cross links. However, a few cross links are

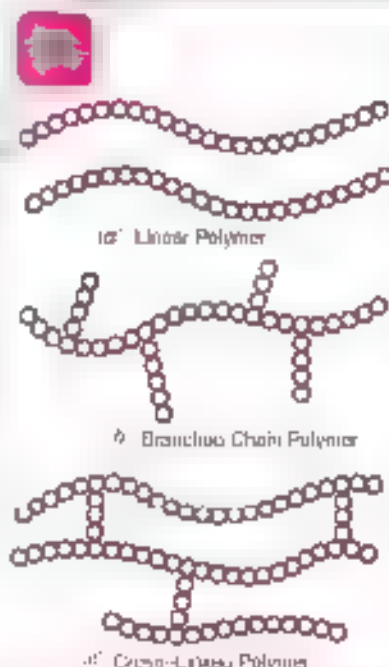
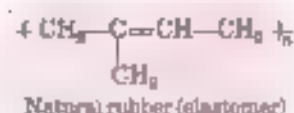


Fig. 1. Different structures of polymers.
a. Linear structure
b. Branched chain structure
c. Cross-linked structure.



* A material like rubber that can return to its original shape after stretching is said to be elastic.

introduced in the chains. For example, natural rubber is a gummy material which has poor elasticity. It becomes soft and sticky when heated and becomes permanently deformed when stretched. However, when natural rubber is heated with 3–5% sulphur, it becomes non-sticky and more elastic. This process is called **vulcanization** and it was discovered by Charles Good Year in 1839. The product formed is called **vulcanized rubber** which has better tensile strength, elasticity and resistance to abrasion than natural rubber. This is due to sulphur cross links between polymer chains. Thus, cross links are introduced in natural rubber to

- impart the property of regaining the original position after stretching force is released.

• prevent the chains from slipping past each other when force is applied.

The examples of elastomers are **buna-S, buna-N, neoprene** etc.

2. Fibres

These are the polymers which have strong intermolecular forces between the chains. These forces are either hydrogen bonds or dipole-dipole interactions. For example, in case of polyamides such as nylon, the intermolecular forces are hydrogen bonding while in polyesters such as terylene or dacron, etc., the intermolecular forces are dipole-dipole interactions between polar carbonyl ($\text{C}=\text{O}$) groups and between carbonyl and cyano ($\text{C}=\text{N}$) groups respectively. Because of strong forces, the chains are closely packed and thus, impart crystalline nature. As a result, the polymers have high tensile strength and less elasticity. Therefore, these polymers have sharp melting points. These polymers are long, thin and thread like and can be woven in fabrics. Therefore, these are used for making fibres.

The common examples are **nylon-6, 6, terylene, silk**, etc.

3. Thermoplastics

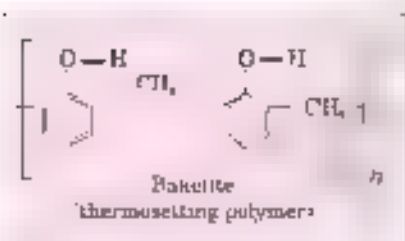
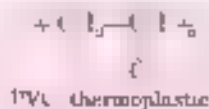
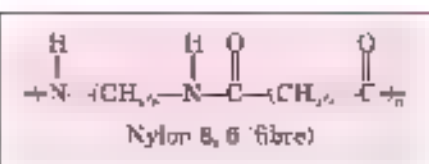
These are the polymers which can be easily softened repeatedly when heated and hardened when cooled with no change in their properties. The intermolecular forces of these polymers are intermediate between those of elastomers and fibres. There is no cross linking between the chains. The softening occurs as the polymer chains move more and more freely because of absence of cross links. When heated, they melt and form a fluid which can be moulded into any desired shapes and then cooled to get the desired product.

Common examples of thermoplastics are **polythene, polystyrene, polyvinyl chloride, teflon**, etc.

4. Thermosetting polymers

These are the polymers which undergo permanent change on heating. On heating, they undergo extensive cross linking between different polymer chains to give a three dimensional network. As a result, they become hard and infusible; therefore, they cannot be reused. They are generally prepared from low molecular mass semi fluid substances. When heated, they get highly cross linked to form hard, infusible and insoluble products. The cross links hold the molecules in place so that heating does not allow them to move freely. Therefore, a thermosetting plastic is cross linked or heavily branched molecule and is permanently rigid.

The common examples are **bakelite, melamine formaldehyde resin** etc.



Basic difference between thermosetting polymers and thermoplastic polymers is that the thermoplastic polymers can be softened repeatedly by heating and can be heated on cooling without change in properties. On the other hand, thermosetting plastics can be heated only once because it undergo permanent change on melting and sets into a new solid which cannot be remelted. Therefore, thermoplastics can be moulded to any desired shape and can be processed again and again. But thermosetting materials cannot be moulded easily into desired shape and cannot be reprocessed. To form articles with the desired shapes from thermosetting materials, the cross linking must be allowed to occur during the fabrication of the article.

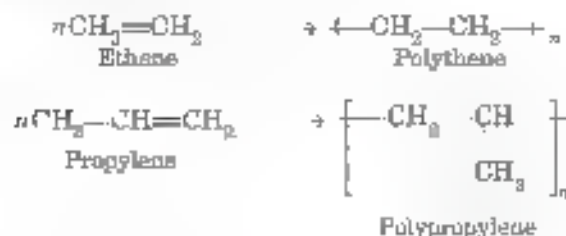
D Classification of Polymers on the Basis of Mode of Synthesis

On the basis of mode of synthesis, the polymers may be classified as

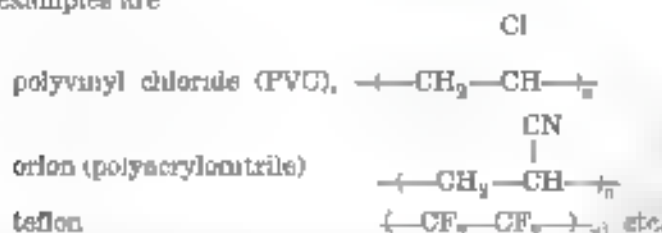
1. Addition polymers, 2. Condensation polymers.

1. Addition polymers

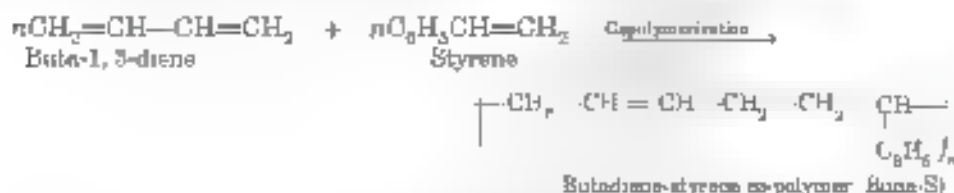
A polymer formed by direct addition of repeated monomers without the elimination of by product molecules is called **addition polymer**. In this type the monomers are unsaturated compounds possessing double or triple bonds. The addition polymers have the same empirical formula as their monomers. For example the addition polymers polythene, polyethylene or polypropylene are obtained as



Other examples are

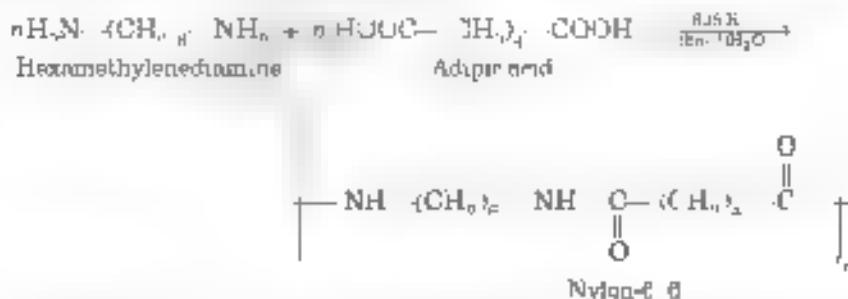


The polymers made by the addition or polymerisation of two different monomers are called **co-polymers**. For example, **Buna-S, Buna-N**, etc.



2. Condensation polymers

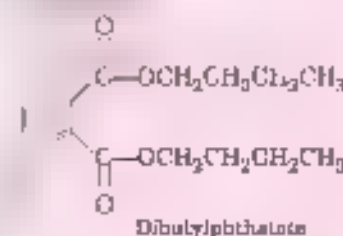
A polymer formed by the condensation of two or more than two monomers with the elimination of simple molecules like water, ammonia, hydrogen chloride, alcohol etc. is called **condensation polymer**. In this type the monomers generally have different bifunctional or trifunctional groups. For example nylon-6, 6 is obtained by the condensation of ω -monomers, hexamethylenediamine and adipic acid with the loss of water molecules.



Some other examples of condensation polymers are *terylene*, *bakelite*, *alkyl resins* etc.

NOTE

◆ **Plasticizers.** Certain plastics do not soften very much on heating. These can be easily softened or made flexible by the addition of some organic compounds which are called **plasticizers**. For example polyvinyl chloride (PVC) is very stiff and hard but it is made soft and rubbery by adding *n*-butyl phthalate as a plasticizer.



Some other common plasticizers are dialkyl phthalates, triethyl triphosphates, $\text{CH}_3-\text{C}_6\text{H}_4-\text{O}-\text{C}_2\text{H}_5$

Differences between addition polymers and condensation polymers.

Addition polymers	Condensation polymers
1. Different monomers add to form a polymer having same molecular formula of the repeating structural unit as that of starting monomer.	A large number of monomers combine with the loss of simple molecules (H_2O , NH_3 , HCl , ROH) to form a polymer having molecular formula of the repeating structural unit different than that of starting monomers.
2. Nothing is lost during polymerisation.	Small molecules like H_2O , NH_3 , HCl , ROH are lost.
3. Generally involves one monomer.	Involves two monomers.
4. The monomers are generally unsaturated compounds.	The monomers generally contain two functional groups.
5. Common examples are polystyrene, polypropylene, PVC, etc.	Common examples are nylon-66, styrene isobutene, etc.

TYPES OF POLYMERISATION REACTIONS

The polymerisation reactions are in the following two principal types

- Addition polymerisation or chain growth polymerisation.
- Condensation polymerisation or step growth polymerisation.

ADDITION POLYMERISATION OR CHAIN GROWTH POLYMERISATION

Addition polymers are formed by the combination of monomers without the elimination of small by product molecules. The monomers used in addition polymers are unsaturated compounds such as alkenes, alkadienes and their derivatives. This polymerisation process involves a series of reactions each of which consists a reactive particle and produces another similar particle resulting a chain reaction. The polymerisation reaction is also called **chain polymerisation** or **chain growth polymerisation** because it takes place through stages leading to increase in chain length and each stage produces reactive intermediates for use in the next stage of the growth of the chain. Like other chemical reactions, this type of polymerisation reaction also involves an initiator which may be a **free radical**, a **cation** or **anion**. Depending upon the nature of the reactive species involved, the addition polymerisation occurs by the following three mechanisms:

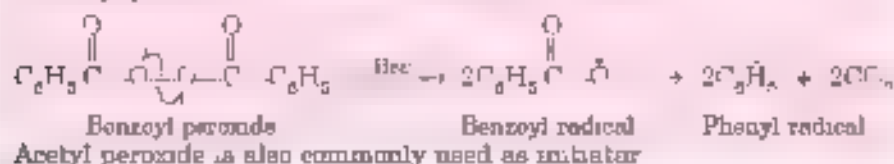
- Free radical addition polymerisation
- Cationic polymerisation
- Anionic polymerisation

However, the free radical addition polymerisation is most common and is discussed below.

Mechanism of Free Radical Addition Polymerisation

A variety of unsaturated compounds such as alkenes or dienes or their derivatives are polymerised by free radical addition polymerisation in the presence of a free radical generating initiator/catalyst like *benzoyl peroxide*, *acetyl peroxide*, *tert-butyl peroxide* etc. This type of polymerisation is performed by heating the monomer with a small amount of initiator (commonly peroxides) or by exposing the monomer to light.

tert-Butyl peroxide and benzoyl peroxide are commonly used initiators because they decompose under mild conditions to form free radicals.

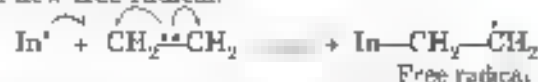


The reaction involves the following steps

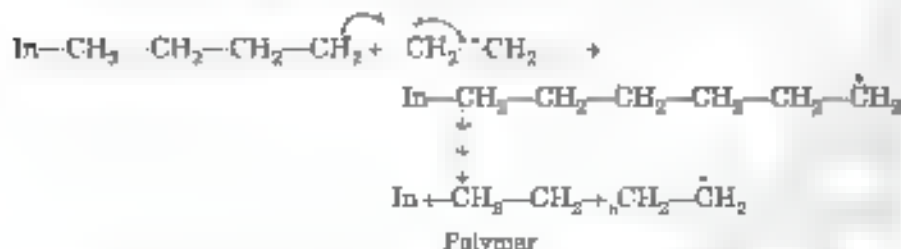
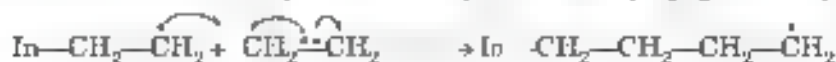
(i) **Chain initiation.** Organic peroxides undergo homolytic fission to form free radicals which act as initiator (In^\bullet).



The initiator (In^\bullet) adds to the carbon-carbon double bond of an alkene molecule to form a new free radical.



(ii) **Chain propagation.** The new free radical adds to a double bond of monomer to form a larger free radical. The radical formed adds to another alkene molecule to form an even larger free radical. This process continues until the radical is destroyed. These steps are called propagation steps.



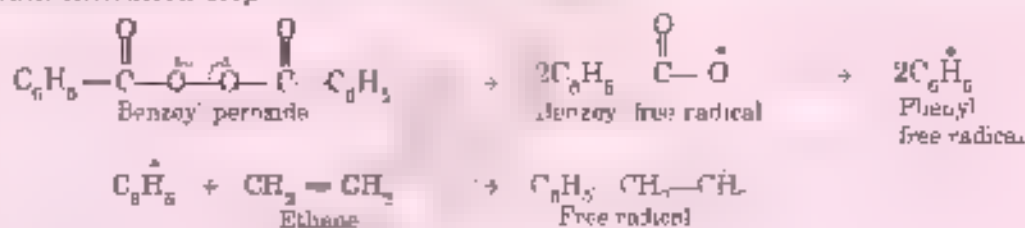
Above steps are repeated until finally polymer is obtained.

(iii) **Chain termination.** The above chain reaction terminates when the two free radicals combine. For example,

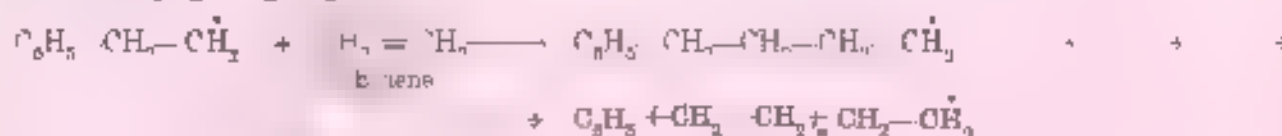


All the steps for polymerisation of ethene in the presence of benzoyl peroxide are shown below.

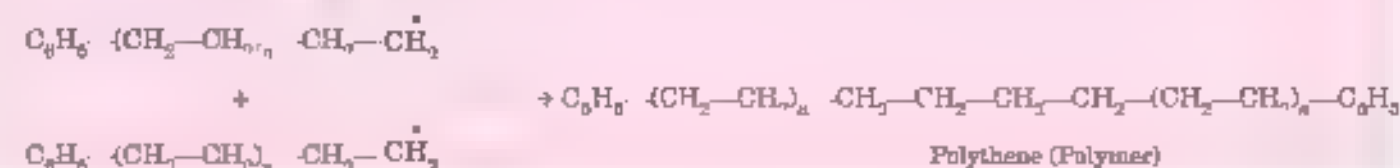
Chain initiation step



Chain Propagating steps



Chain terminating steps



COMPETITION PLUS

Certain alkene monomers can be polymerised by a cationic mechanism or anionic mechanism.

For detail refer Competition File (page 34).

SOLVED EXAMPLES

□ **Example 1.**

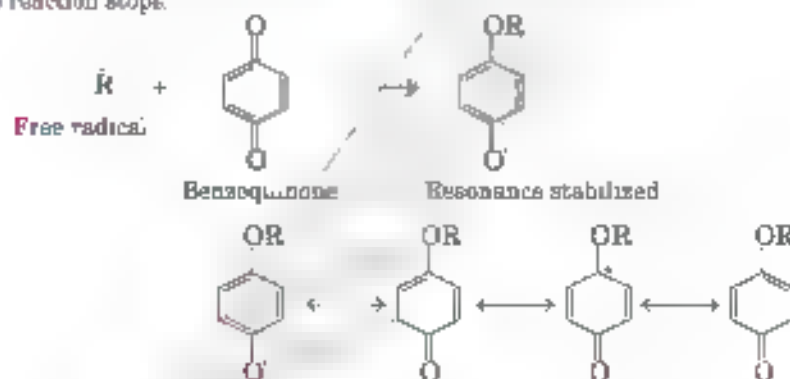
Is $-\text{NH}-\text{CHR}-\text{CO}-$ a homopolymer or a copolymer? [M.C.E.T.]

Solution: It is a homopolymer because the repeating structural unit has only one type of monomer i.e. $H_2N-CHR-COOH$.

□ **Example 2.**

How does the presence of benzoyl peroxide inhibit the free radical polymerization of a vinyl derivative?

Termination Benzoquinone combines with free radical intermediate to form a non-reactive radical, which is highly stabilized by resonance. Because of the lack of reactivity of the new radical formed, it inhibits the further progress of the chain reaction. Therefore, the reaction stops.



PREPARATION OF SOME IMPORTANT ADDITION POLYMERS

1. Polyethylene or Polythene

There are two types of polythene as

- (a) Low density polythene (LDP) (b) High density polythene (HDP)

Both of these are obtained from ethene and have the same repeating structure, unit i.e., $-\text{CH}_2-\text{CH}_2-$ as discussed below

(a) **Low density polythene (LDP).** It is manufactured by heating pure ethylene to 850-570 K under high pressure 1000-2000 atm in the presence of traces of oxygen (0.08 to 0.1%) or peroxide initiator (catalyst, which initiates polymerisation).



It is obtained through the free radical addition and hydrogen atom abstraction. It consists of highly branched chain molecules. Due to branching the polythene molecules do not pack well and therefore, it has low density (0.92 g cm^{-3}) and low melting point (384 K). Low density polythene is chemically inert and tough but flexible and a poor conductor of electricity.

Uses: It is used

- (i) as a packing material in the form of thin plastic film bags
- (ii) for insulation of electricity carrying wires and cables,
- (iii) in the manufacture of flexible pipes, toys, squeeze bottles, etc.

(b) **High density polythene (HDP).** It is prepared by heating ethene in a hydrocarbon solvent at about 333–343 K under a pressure of 6–7 atmospheres in the presence of a catalyst such as triethylaluminum and titanium tetrachloride known as Ziegler-Natta catalyst.



This polymer consists of linear chains and therefore, the molecules can closely pack in space. It has therefore, high density (0.97 g/cm^3) and higher melting point (403°K). It is quite harder, tougher as it has greater tensile strength than low density polythene. It is also chemically inert.

Uses. It is used

- (i) in the manufacture of containers (buckets, tubes, dustbins, etc.),
- (ii) for the manufacture of different housewares, pipes, etc.

2. Polytetrafluoroethylene (Teflon or PTFE). It is an addition polymer of tetrafluoroethene. It is obtained by heating tetrafluoroethene with a free radical or persulphate catalyst ammonium persulphate, $\text{NH}_4)_2\text{S}_2\text{O}_8$, at high pressures.



It is very tough material and is chemically inert. It is resistant to acids, heat and attack by corrosive reagents such as acids and bases. It is a good conductor of electricity.

Uses. It is used

- (i) as a material resistant to heat and chemical attack,
- (ii) for coating articles and cookware to make them non-sticky or non-stick utensils,
- (iii) for making gaskets, pump packings, valves, air-seals, non-lubricated bearings, etc.

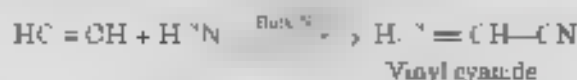
3. Polyacrylonitrile (PAN) or Orlon. It is a polymerised product of vinyl cyanide (acrylonitrile). It is obtained by addition polymerisation of acrylonitrile in the presence of a peroxide catalyst.



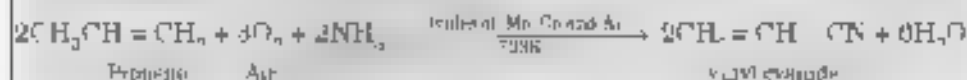
Vinyl chloride ($\text{CH}_2=\text{CHCl}$) and vinylidene chloride ($\text{CH}_2=\text{CCl}_2$) gives a copolymer **Saran** which is used as a film for wrapping food.

Teflon coatings undergo decomposition at temperature above 600°C .

The monomer, vinyl cyanide can be prepared by treating acetylene with HCN in the presence of $\text{Ba}(\text{CN})_2$ or CuCl-HCl catalyst:



It can also be prepared by passing a mixture of propene, ammonia and air over a catalyst consisting of a mixture of oxides of molybdenum, cobalt and alumina at 723°K .



It is a hard, horny and high melting substance. It is also known as **acrilan** or **orlon**.

Uses. It is used

- (i) as a substitute of wool for making blankets, sweaters, bathing suits, etc.,
- (ii) for making synthetic carpets.

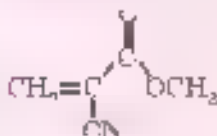
CONDENSATION POLYMERS

These are formed by the condensation of two or more bifunctional monomers with the elimination of simple molecules like water, ammonia, alcohol, etc. In these reactions, the product of each step is again a bifunctional species and the sequence of condensation goes on. Since, each step produces a distinct functionalised species and is independent of each other, this process is also called

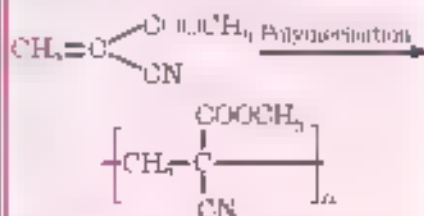
R U Curious...

□ What is super glue or crazy glue?

► Super glue or crazy glue is a polymer of methyl α -cyanoacrylate



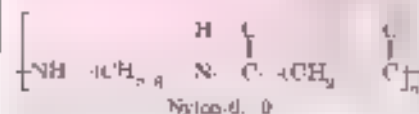
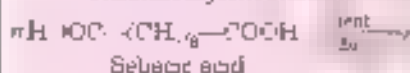
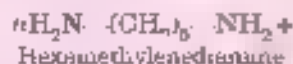
Due to the presence of two electron withdrawing groups (CN and COOCH₃), it undergoes polymerisation very quickly. It is one of very strong fast-acting adhesives of medical and household uses.



Cyanoacrylate adhesives are sometimes known as **instant glues**.

NOTE

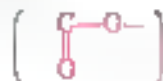
There is another commonly used nylon known as nylon-6, 10 (nylon six-ten). It is a polymer of hexamethylenediamine (six carbon atoms) and sebacic acid (ten carbon atoms).



as **step growth polymerisation**. Some common examples of condensation polymers are

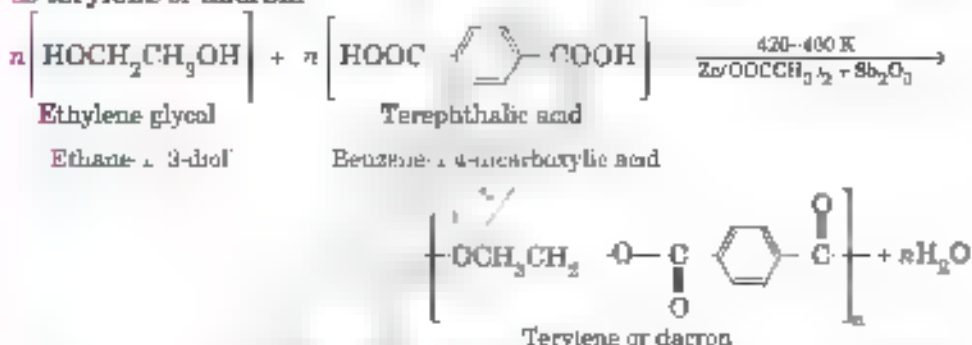
1. Polyesters

These are poly condensation products of dicarboxylic acids and diols. These involve **ester linkages**



For example,

(i) **Terylene**. It is a polymer of **ethylene glycol** (ethane-1,2-diol) and **terephthalic acid** (benzene-1,4-dicarboxylic acid). It is obtained by heating a mixture of ethylene glycol and terephthalic acid at 420° to 460° K in the presence of zinc acetate-antimony trioxide, $[\text{Zn}(\text{OOCCH}_3)_2 + \text{Sb}_2\text{O}_3]$, catalyst. It is known as **terylene** or **dacron**.

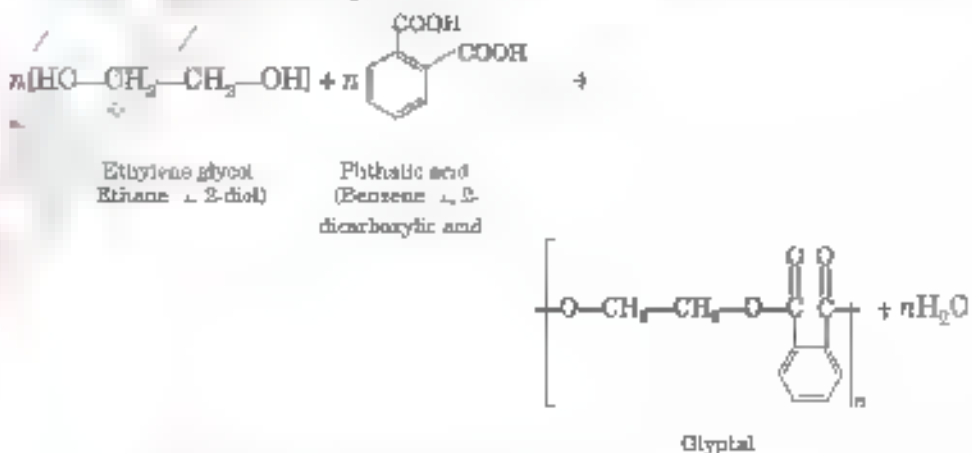


It is a very strong fibre. It is highly crease-resistant, durable and has low moisture content. It is also not damaged by pests like moths and mildew.

Uses. It is used

- in blending with cotton or wool fibres because it is crease resistant.
- as glass reinforcing materials in safety helmets.
- for making magnetic recording tapes.

(ii) **Glyptal**. It is a polymer of ethylene glycol (ethane-1,2-diol) and phthalic acid (benzene-1,2-dicarboxylic acid).



It is a network cross-linked polymer

- in manufacture of paints and lacquers.
- for making building materials such as asbestos, cement, etc.

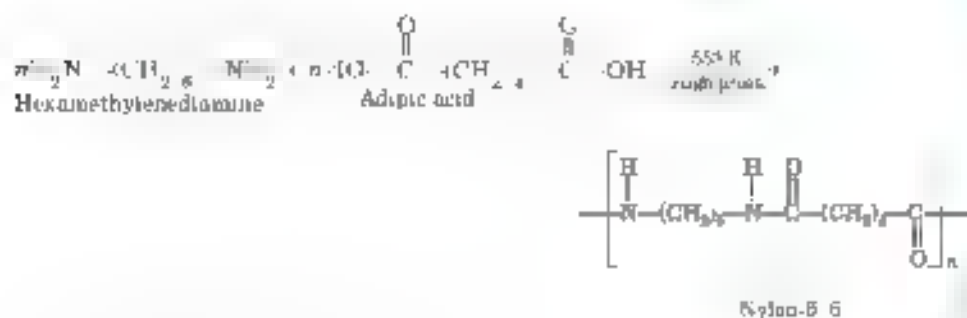
2. Polyamides

These have amide linkages $\left(\text{C}-\text{N} \right)$ in the chain. These polymers are

popularly known as **nylons**.

For example nylon-6,6 reads as nylon six six and nylon-6 reads as nylon six

(f) **Nylon-6,6.** The monomer units of Nylon-6,6 are **hexamethylenediamine** and **adipic acid**. It is prepared by the condensation of hexamethylene diamine with adipic acid under high pressure and high temperature.



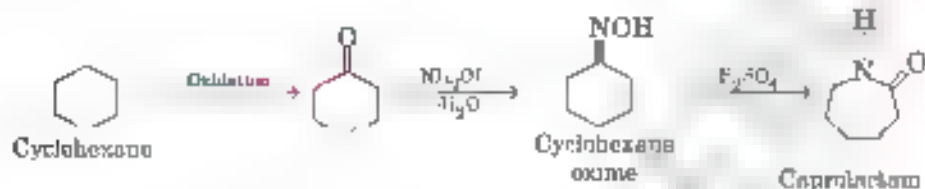
Uses. It is used

in making crates for brushes.

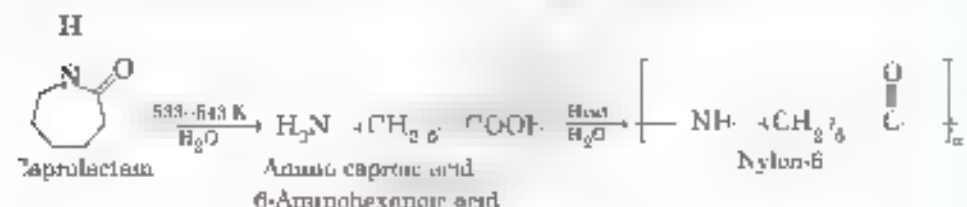
ii) in textiles and also for making sheets. It is blended with wool to make socks and sweaters.

(iii) in the manufacture of cords and climbing ropes

(iv) **Nylon-6.** It has the monomer **caprolactam** which is obtained from **cyclohexane**



Coproductum on heating with traces of water gives ϵ -amino caproic acid which is a mono-carboxylic amino acid containing six carbon atoms. This polymerises to give nylon-6.



Uses. It is used in the manufacture of tyre cords, fabrics and ropes.

3. Formaldehyde removal

These include polymers like bakelite and melamine polymers.

(i) **Phenol formaldehyde resins (bakelite)**. It is a condensation polymer and is obtained from **phenol** and **formaldehyde** in the presence of either an acid or a base catalyst. The process actually involves the initial formation of *o*- and/or *p*-hydroxymethylphenol derivatives. These react further with phenol to form compounds having methylene (CH_2) bridges either at *ortho* or *para* position or both at *ortho* and *para* positions with respect to phenolic group. The initial product is a linear product called **novolac** which is also used as a paint. Thus on further heating with formaldehyde undergoes cross linkages to form infusible solid called bakelite.

**SOME MORE IMPORTANT
QUESTIONS**

- **Kevlar**

is a polyamide obtained by the condensation polymerization of terephthalic acid and *p*-phenylenediamine (1 + 1 molar ratio).

The fibres of this polymer are very strong and are used to make light weight bullet-proof vests.

- **Nomex**

is a polyamide obtained by condensation of *m*-phthalic acid and *m*-chloro benzene.

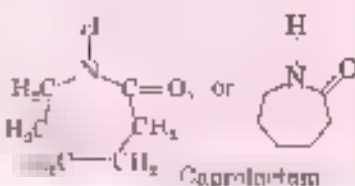
It has fire resistant properties and is used in protective clothing for fire-fighters, astronauts, and race-car drivers.

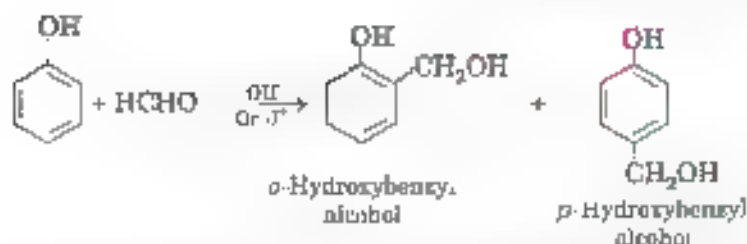
- **Lelayn**

a polycarbonate or polyester obtained by the condensation of diethylcarbonate and bisphenol A

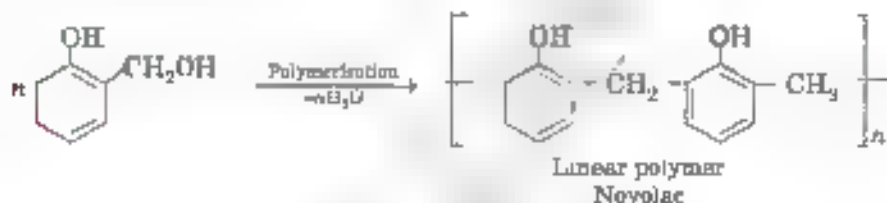
It has unusually high impact strength and is used for bullet-proof windows and safety or crash helmets.

Caprolactam is a seven membered cyclic amide (cyclic amides are known as lactams).

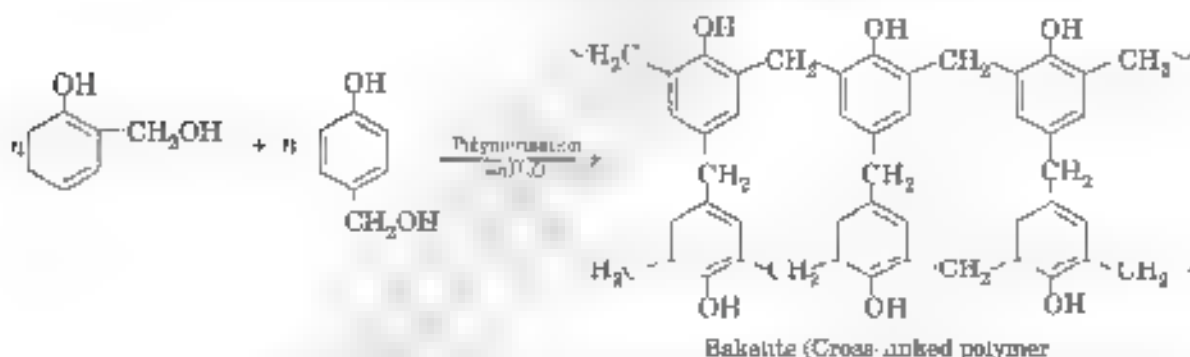




The condensation of o-hydroxybenzyl alcohol or p-hydroxybenzyl alcohol gives a *linear polymer*



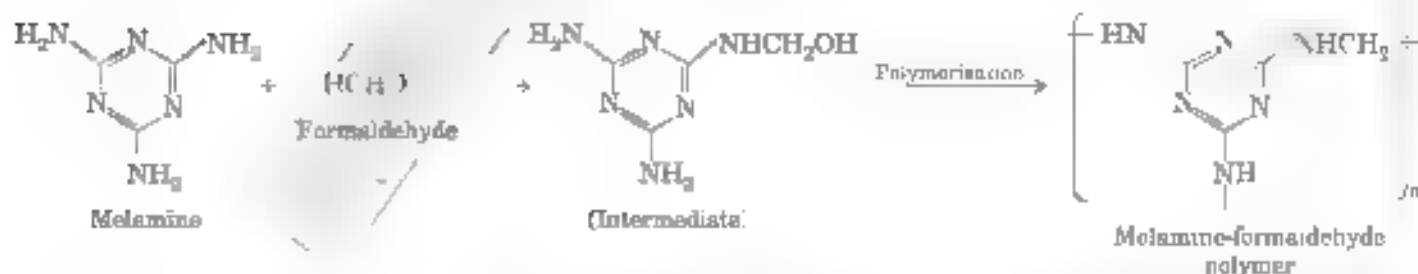
The *ortho* and *para* substituted phenols can undergo polymerisation to produce a cross-linked polymer known as *bakelite*. Novolac on heating with formaldehyde also undergoes cross linkages to form bakelite.



Uses. Soft bakelites with low degree of polymerisation are used for making glue for binding laminated wooden planks and varnishes. High degree of polymerisation gives hard bakelites which are used for making combs, fountain pens, barrels, phonograph records, electrical switches and handles of various utensils, formica table tops and many other products.

4. Melamine formaldehyde resin.

It is a polymer formed by the condensation of melamine which is a heterocyclic triamine with formaldehyde. The polymerisation occurs as

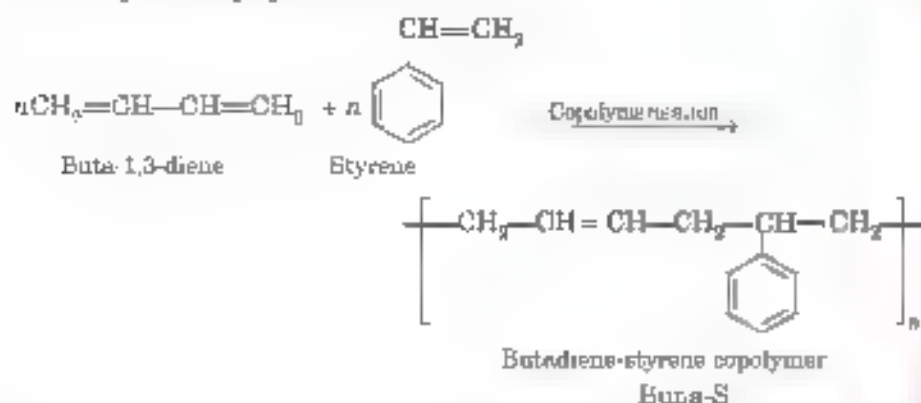


Uses. It is used in making unbreakable crockery. These are used for making cups and plates which are quite hard and durable. They do not break on being dropped.

CO-POLYMERISATION AND CO-POLYMERS

We have already learnt that polymers made up of same repeating units are called **homopolymers** and polymers obtained from two or more different monomer units are called **copolymers**. The copolymers can be made by chain growth polymerisation as well as step growth polymerisation. It contains multiple units of each monomer used in the same polymeric chain. For example,

a mixture of buta-1,3-diene and styrene can form a co-polymer known as butadiene-styrene co-polymer called buna-S.



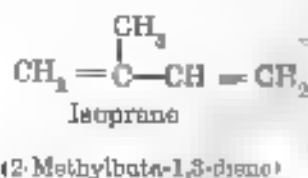
Co-polymers have properties quite different from the homopolymers. For example, polystyrene, a homopolymer of styrene is a good electrical insulator and is moulded into toys, comb, radio and television parts etc. But, styrene (25%) and buta-1,3-diene (75%) a co-polymer is very tough and is a good substitute for natural rubber. It has high abrasion resistance, high loading capacity and is used for the manufacture of auto tyres. Its other uses are in floor tiles, footwear components, cable insulation, etc. Many co-polymers formed from condensation reactions are also known.

NATURAL AND SYNTHETIC RUBBERS

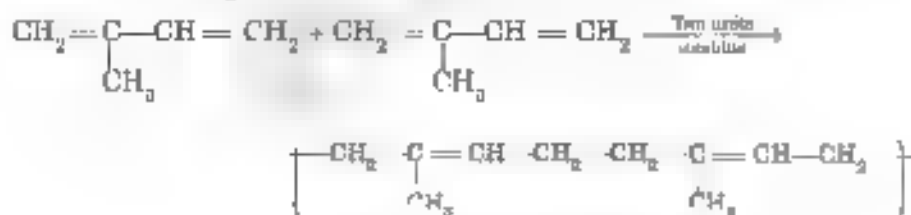
A. NATURAL RUBBER

Rubber is a naturally occurring polymer. It is obtained as latex from rubber trees. Rubber latex is a colloidal suspension of rubber in water. Rubber trees are found in tropical and semi-tropical countries such as India, southern part of Malaysia, Indonesia, Ceylon, South America, etc. It is highly elastic. It can be easily deformed but regains its original shape after the stress is relieved. Therefore, it is also termed as elastomer. This elasticity makes it a valuable for a variety of uses.

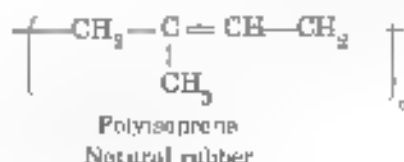
Natural rubber is a polymer of isoprene (2-methylbuta-1,3-diene).



In natural rubber, about 1000 C_4H_8 isoprene units are linked together in a chain like arrangement as shown below.

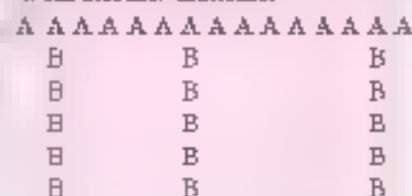


When n isoprene units combine, the polymer has the formula



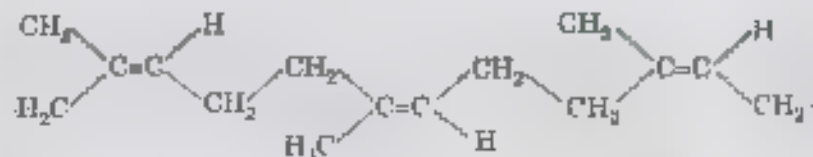
Copolymers are of four types depending upon the distribution of monomer units in the chain.

- **Alternating copolymers** in which two monomers alternate.
A B A B A B A B A B A B
- **Block copolymers** in which there are blocks of each kind of monomer alternating with each other.
A A A B B B A A A B B B A A A B B B
- **Random copolymers** in which the distribution of monomers is random.
A A B A B B A B A A B B A A B A A B
- **Graft copolymers** which contain branches derived from one monomer grafted onto the backbone derived from another monomer.



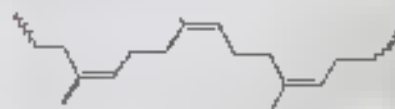
These structural differences extend the range of physical properties available to chemists for designing a copolymer.

It may be noted that natural rubber is *cis*-1,4-polyisoprene and has an *cis* configuration about the double bond as shown below



All *cis* configuration

There are weak van der Waals forces and therefore it is a natural non-crystalline. However, the *cis* configuration has highly regular zig-zag chains which fit together well. The *cis* \rightarrow *trans* isomerization occurs naturally as *gutta percha* which is highly crystalline and non-elastic because of packing of chains. Extended chains of natural rubber and *gutta percha* are shown below



all *cis* configuration in natural rubber



all *trans* configuration in gutta percha

Vulcanization of Rubber

Natural rubber becomes soft and sticky when heated at high temperatures ($>335\text{ K}$) and brittle at low temperatures ($< 289\text{ K}$). It shows high water absorption capacity. It is soluble in non-polar solvents and is non-reactant to attack by oxidising agents. It is not hard and tough. The properties of natural rubber can be modified and improved by the process of vulcanization. To improve its properties, it is heated with sulphur at a temperature of 373 to 415 K. The process of heating natural rubber with sulphur to improve its properties is called **vulcanization**. The vulcanization process performed originally was slow. Nowadays, some additives such as zinc oxide etc. are used to accelerate the rate of vulcanization. During vulcanization, sulphur cross links are formed (Fig. 3). The formation of cross-links makes rubber hard, tough with greater tensile strength. The vulcanized rubber has excellent elasticity, low water absorption tendency, resistance to oxidation and organic solvents. The double bonds in the rubber molecule act as reactive sites. The allylic $-\text{CH}_2-$ alpha to double bond is also very reactive. During vulcanization, sulphur forms cross-links either at their reactive allylic sites or at the sites of the double bonds (Fig. 3). As a result, rubber gets stiffer and intermolecular movement of rubber springs is prevented resulting in physical character of rubber. The extent of stiffness of vulcanized rubber depends upon the amount of sulphur added. For example, about 5% sulphur is used for making tyre rubber while 80% of sulphur is used for making battery case rubber.

In vulcanized rubber, the chains are normally tangled up with each other (Fig. 4 (a)). When the rubber is stretched, the chains straighten out to some extent (Fig. 4 (b)). The chains cannot slip past each other because of the polysulphide bridges. Thus, rubber can be stretched only to a limited extent. When the tension is removed, the chains try to coil up again and the rubber resumes its original shape.

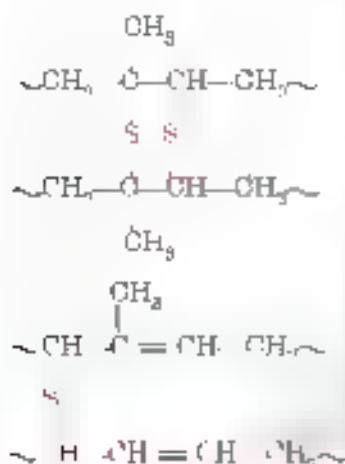


Fig. 3. Sulphur cross links in vulcanized rubber

Highly vulcanized rubber containing large amount (30-40%) of sulphur is called **ebonite**.

It is hard, relatively inelastic rubber used for combs, buttons, electrical insulation etc.

The comparison of the main properties of natural rubber and vulcanized rubber are given below

Natural rubber	Vulcanized rubber
1. Natural rubber is soft and sticky	Vulcanized rubber is hard and non-sticky
2. It has low tensile strength.	It has <u>high</u> tensile strength
3. It has low elasticity.	It has <u>high</u> elasticity
4. It can be used over a narrow range of temperature (from 10°C to 60°C).	It can be used over a wide range of temperature i.e. 40°C to 100°C.
5. It has low wear and tear resistance.	It has <u>high</u> wear and tear resistance
6. It is soluble in solvents like ether, carbon tetrachloride, petrol etc.	It is <u>insoluble</u> in all the common solvents.

B. SYNTHETIC RUBBERS

The **synthetic rubber** is any vulcanisable rubber like polymer which is capable of getting stretched to about twice of its length. However, it returns to its original shape and size as soon as the external stretching force is released. It is obtained by polymerizing certain organic compounds which may have properties similar to rubber and some additional desirable properties. Most of these polymers are derived from butadiene derivatives and contain carbon-carbon double bonds. These are also vulcanised by processes developed for natural rubber. Therefore, the synthetic rubbers are either homopolymers of 1,3-butadiene or co-polymers in which one of the monomers is 1,3-butadiene or its derivative so that the polymer has the availability of double bonds for its vulcanization.

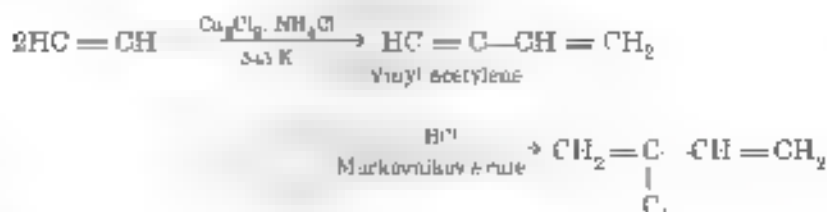
Some common examples of synthetic rubbers are neoprene, styrene butadiene rubber (SBR), thiolol, silicones, polyurethane rubber, etc.

1. Neoprene Rubber

It is prepared by free radical polymerisation of chloro-styrene (2-chlorobuta-1,3-diene).



The starting material, chloroprene, obtained by dimerization of acetylene by passing it through aqueous solution of NH_4Cl and cuprous chloride at 343K followed by treatment with HCl .



Uses: Neoprene is superior to natural rubber in its stability to aerial oxidation and its resistance to vegetable and mineral oils, gasoline and other solvents. It is used as material for making conveyor belts, gaskets, hoses and printing rollers.

2. Styrene Butadiene Rubber (SBR or Buna-S)

I. is obtained by the polymerisation of buta-1, 3-diene and styrene in the ratio of 3 : 1 in the presence of sodium.

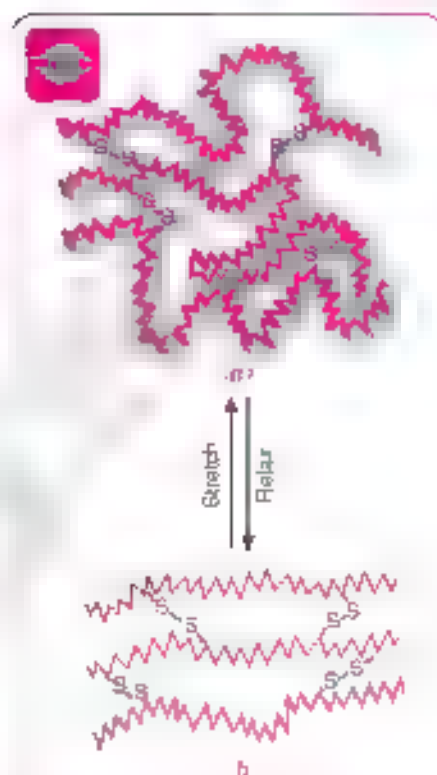
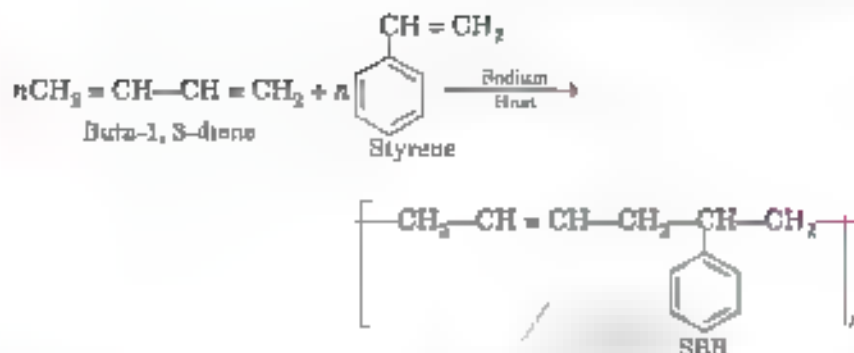


Fig. 4. Vulcanized rubber and effect of stretching

In Buna-S, Bu stands for butadiene, Na for sodium and S for styrene.

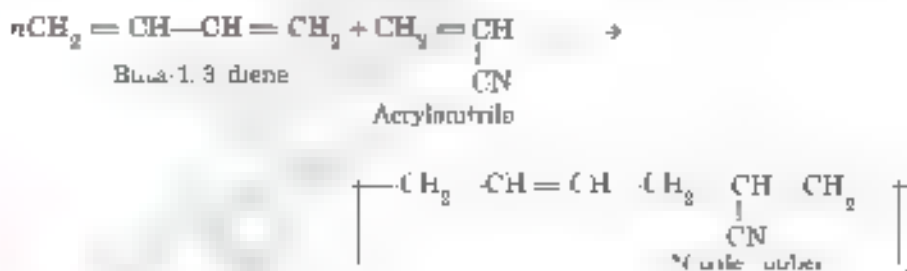


It is also called Buna-S, in which Bu stands for butadiene, Na for sodium and S stands for styrene. It has slight tensile strength than natural rubber.

Uses: It is used for making automobile tyres. It is also used for making floor tiles, footwear components, cable insulation, etc.

3. Nitrile rubber or Buna-N

It is obtained by polymerisation of buta-1,3-diene and acrylonitrile in the presence of a peroxide catalyst.



The letter 'N' in Buna-N stands for acrylonitrile.

It is also called, Buna-N. It is resistant to the action of petrol, lubricating oil and organic solvents.

Uses: It is used for making machine's, manufacture of hoses, tank linings etc.

MOLECULAR MASSES OF POLYMERS

A polymer sample contains chains of varying lengths and therefore, its molecular mass is always expressed as an average. On the other hand, natural polymers such as proteins contain chains of identical length and, therefore, they have definite molecular mass.

The molecular mass of a polymer can be expressed in two ways

(i) **Number average molecular mass (\bar{M}_n)**

If N_1, N_2, N_3, \dots are the number of molecules with molecular masses M_1, M_2, M_3, \dots respectively, then the number average molecular mass is

$$\bar{M}_n = \frac{N_1 M_1 + N_2 M_2 + N_3 M_3 + \dots}{N_1 + N_2 + N_3 + \dots}$$

This may be expressed as

$$\bar{M}_n = \frac{\sum N_i M_i}{\sum N_i}$$

where N_i is the number of molecules of the i th type with molecular mass M_i .

(ii) **Weight average molecular mass (\bar{M}_w)**

If w_1, w_2, w_3, \dots are the masses of species with molecular masses M_1, M_2, M_3, \dots respectively, then the weight average molecular mass is

$$\bar{M}_w = \frac{w_1 M_1 + w_2 M_2 + w_3 M_3 + \dots}{w_1 + w_2 + w_3 + \dots}$$

$$\begin{aligned} \text{or } \bar{M}_n &= \frac{\sum m_i M_i}{\sum m_i} \\ \text{But } m_i &= N_i M_i, \text{ so that} \\ \bar{M}_n &= \frac{\sum N_i M_i^2}{\sum N_i M_i} \end{aligned}$$

where N_i is the number of molecules of mass M_i

Polydispersity index

The ratio of mass average molecular mass to the number average molecular mass is called **polydispersity index, PDI**.

$$PDI = \frac{\bar{M}_w}{\bar{M}_n}$$

This gives an idea about the homogeneity of a polymer

i) The polymers whose molecules have nearly same molecular masses are called **monodisperse polymers**. For these molecules $\bar{M}_w = \bar{M}_n$ and therefore, **PDI is one**.

ii) The polymers whose molecules have wide range of molecular masses are called **polydisperse polymers**. For these polymers, $\bar{M}_w > \bar{M}_n$ and therefore, their **PDI is greater than one**.

Thus, it may be concluded that in general, **natural polymers are more homogeneous than synthetic polymers**.

For natural polymers, PDI is usually unity and therefore, natural polymers are **monodisperse**.

For synthetic polymers, the PDI is greater than unity and therefore, \bar{M}_w is always greater than \bar{M}_n . \bar{M}_n is always determined by employing methods which depend upon the number of molecules present in the polymer sample. For example colligative property such as osmotic pressure is used. On the other hand, weight average molecular mass is measured by using the methods such as light scattering and ultracentrifugation, sedimentation, etc. which depend upon the mass of individual molecules.

WORKED EXAMPLES

□ Example 1.

In a polymer sample 30% molecules have a molecular mass 20,000, 40% have molecular mass, 30,000 and the rest have 60,000. Calculate mass average and number average molecular masses.

Solution The polymer contains 30% molecules of mass 20,000, 40% molecules of molecular mass 30,000 and rest 30% of molecules of molecular mass 60,000. Thus,

$$\begin{aligned} \bar{M}_n &= \frac{\sum N_i M_i}{\sum N_i} \\ &= \frac{30 \times 20000 + 40 \times 30000 + 30 \times 60000}{30 + 40 + 30} = 36000. \end{aligned}$$

$$\begin{aligned} \bar{M}_w &= \frac{\sum N_i M_i^2}{\sum N_i M_i} \\ &= \frac{30(20000)^2 + 40(30000)^2 + 30(60000)^2}{30 \times 20000 + 40 \times 30000 + 30 \times 60000} = 43333. \end{aligned}$$

BIODEGRADABLE POLYMERS

The polymers are finding extensive use in our day to day life. However, a large number of polymers are quite resistant to the environmental degradation process and are therefore, responsible for the accumulation of polymeric solid waste materials. These solid wastes cause acute environmental problems and remain undegraded for quite a long time. With the increasing use of polymers, the problem of disposal of waste of these products is also posing serious problem. The main option is to produce biodegradable polymers which can be broken down rapidly by soil micro-organisms and therefore, do not cause any serious effects on the environment. Thus,

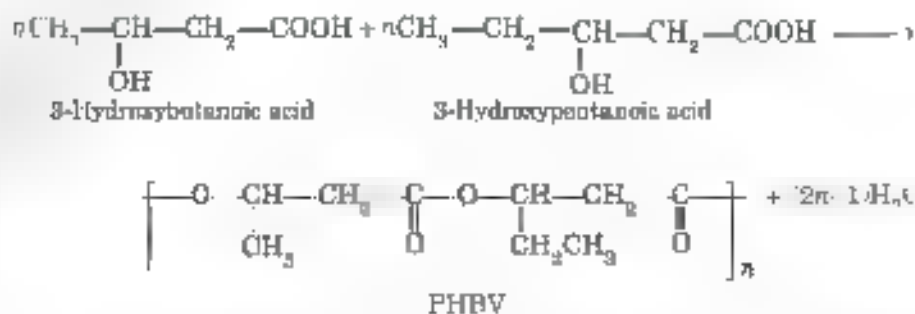
biodegradable polymers are the polymers which are degraded by micro-organisms within a suitable period so that biodegradable polymers and their degraded products do not cause any serious affects on the environment.

In biological systems, biopolymers degrade mainly by enzymatic hydrolysis and to some extent by oxidation. Therefore in view of the disposal problems of polymer waste and for developing polymers for other safe uses in human system, attempts have been made to develop biodegradable synthetic polymers. These synthetic polymers mostly have functional groups which are normally present in biopolymers and lipids.

Among these aliphatic polyesters are one important class of biodegradable polymers which are commercially potential biomaterials. The common examples of biodegradable polymers are polyhydroxy butyrate (PHB), polyhydroxy butyrate-co- β -hydroxy valerate (PHBV), polyglycolic acid (PGA), polylactic acid (PLA), poly- ϵ -caprolactone (PCL) etc. These are briefly discussed below.

1. Poly- γ -hydroxybutyrate-co- β -hydroxy valerate (PHBV)

It is copolymer of β -hydroxybutanoic acid and β -hydroxypentanoic acid, in which the monomer units are joined by ester linkages.


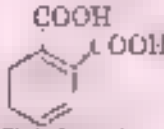



The properties of PHBV vary according to the ratio of both the acids. β -Hydroxy butanoic acid provides stiffness while β -hydroxypentanoic acid gives flexibility to the copolymer. It is used in specialty packaging, orthopaedic devices and in controlled release of drugs. When a drug is enclosed in a capsule of PHBV, it is released only when the polymer is degraded in the body. It also undergoes bacterial degradation in the environment.

2. Polyglycolic acid (PGA)

Polyglycolic acid (PGA) is obtained by the chain polymerisation of cyclic dimer of glycolic acid, $\text{HO}-\text{CH}_2\text{COOH}$.

Table 1. Some other commercially important compounds.

Name of polymer	Monomers	Structure	Important uses
Polypropene	$(\text{H}_2\text{C}=\text{CH}-\text{CH}_3)$ Propene	$\left[\begin{array}{c} \text{CH} - \text{CH}_2 \\ \\ \text{CH}_3 \end{array} \right]_n$	for packaging of <i>textiles and foods</i> (i) for manufacturing covers of bags, lining material for TV cabinets and refrigerators, (ii) for making ropes, fibres, heat shrinkable wraps for records and other articles. (iii) for making automobile mouldings, seat covers, carpet fibres, etc
Polystyrene	$\text{CH}=\text{CH}_2$  Styrene	$\left[\begin{array}{c} \text{C}_6\text{H}_5 \\ \\ \text{CH}_2 - \text{CH} \end{array} \right]_n$	(i) for making hot drink cups, toys, combs, household articles, etc (ii) for making radio and television bodies, refrigerator covers, neon indicator wrapping material. (iii) for making tiles to be used in covering ceiling and floors
Poly(vinyl chloride) (PVC)	$\text{CH}_2=\text{CH}-\text{Cl}$ Vinyl chloride	$\left[\begin{array}{c} \text{H}_2 - \text{CH} \\ \\ \text{Cl} \end{array} \right]_n$	(i) in the manufacture of rain coats, hand bags, curtain clothes, toys, (ii) in artificial flooring, (iii) as a good insulating material in wires and other electrical goods (iv) for making gramophone records
Polymethyl methacrylate PMMA	$\text{CH}_2=\text{C}(\text{COOCH}_3)\text{CH}_3$ Methyl methacrylate	$\left[\begin{array}{c} \text{CH}_2 - \text{C} \\ \quad \\ \text{COOCH}_3 \quad \text{CH}_3 \end{array} \right]_n$	used in the manufacture of lenses transparent domes and sky gls dentures, aircraft windows and protective coatings (ii) Its commercial names are Lucite, Plexiglass, Acrylite and Perspex.
Urea formaldehyde resin	$\text{NH}_2-\text{CONH}_2$ Urea 2. $\text{H}-\text{CHO}$ Formaldehyde	$\left[\text{NH}-\text{CO}-\text{NH}-\text{CH}_2 \right]_n$	For making <i>unbreakable cups, plates, and</i> <i>laminated sheets</i>
Glycol	$\text{HOCH}_2\text{CH}_2\text{OH}$ Ethylene glycol 2.  Phthalic acid	$\left[\text{OOC}-\text{CH}_2\text{OOC} \right]_n$ 	For manufacture of <i>paints and lacquers</i> For manufacture of <i>building materials</i>
Thiokol or polysulphide rubbers	$\text{ClCH}_2\text{CH}_2\text{Cl}$ Ethylene dichloride 2. Na_2S_x Sodium tetrathiolate	$\left[\text{CH}_2 - \text{CH}_2 - \text{S} - \text{S} - \text{S} - \text{S} \right]_n$ Thiokol	have low tensile strength but better resistance to abrasion and solvents and are therefore, used in tyre tread coatings

SOLVED EXAMPLES

Example 4.

Identify a *biodegradable polyester* which is used in packaging and orthopaedic devices

(i) Write its full form.

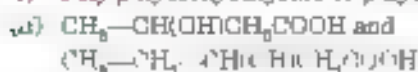
(ii) Give the structures of monomers from which it is formed

(iii) Show the formation of polymer

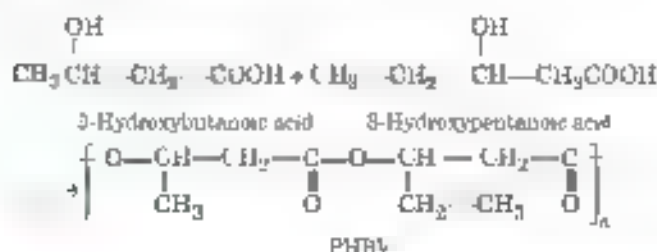
(CBSE Sample Paper 2011)

Solution : It is PHBV

i) Poly β -hydroxybutyrate-co- β -hydroxyvalerate



iii)



Practice Problems

- Arrange the following polymers in increasing order of intermolecular forces. Also classify them as addition and condensation polymers.
Nylon-6, neoprene, PVC
- Classify the following polymers as chain growth and step growth polymers.
Buna-S, Nylon-66, Terylene, PVC
- Fill in the blanks.

Monomers	Polymers	One important use
	Glyptal	for making crockery
Adipic acid, hexamethylene diamine		
ii)		for making switches and plugs
iii)	PMAA	

Answers to Practice Problems

- Neoprene, PVC, nylon-6
Neoprene and PVC Addition polymers
Nylon-6 condensation polymer
- Chain growth polymers are and σ
- i) Ethylene glycol, phthalic acid, manufacture of paints, lacquers
Melamine, formaldehyde, manufacture of formaldehyde resin
Nylon-66 for making carpets and textile fibres
ii) Phenol, formaldehyde, bakelite
iii) Methyl methacrylate for making lenses

add on

Conceptual Questions

Q.1. What is the primary structural feature necessary for a molecule to make it useful in a condensation polymerisation reaction? (A.I.S.B. 2010, Assam S.B. 2013)

Ans. The monomers must be bifunctional i.e. contain two functional groups.

Q.2. What are cross-linked polymers? Give one example of this type.

Ans. The polymers in which the linear polymer chains are cross-linked to form a three-dimensional network structure are called cross-linked polymers. The common example of this type of polymer is bakelite.

Q.3. What is the difference between two notations nylon-6 and nylon-66?

Ans. Nylon-6 is obtained from caprolactam which is obtained from cyclohexane. It has only one compound having only 6-carbon atoms.

Nylon-66 refers to polymer obtained from 6-carbon atoms of dicarboxylic acid (adipic acid) and 6-carbon atoms of diamine (hexamethylene diamine).

Q.4. Are proteins natural or synthetic polymers?

Ans. Proteins are natural polymers.

Q.5. Name one polymer formed by step growth polymerisation. Give names of its monomers.

Ans. Nylon-66. Its monomers are

Adipic acid $\text{HOOC}(\text{CH}_2)_4\text{COOH}$

Hexamethylenediamine $\text{NH}_2(\text{CH}_2)_6\text{NH}_2$

Q.6. What is the trade name of polyacrylonitrile?

Ans. Orlon or acrilon

Q.7. How do thermoplastic differ from thermosetting polymers?

Ans. Thermoplastics when heated become soft. These can be moulded into any desired shape. The thermoplastics can be processed again and again.

On the other hand, thermosetting plastics on heating become hard and insoluble masses. These cannot be moulded into desired shape and cannot be reprocessed.

Q.8. Arrange the following polymers in increasing order of their intermolecular forces. Also classify them as addition and condensation polymers:

Nylon-66, Buna-S, Polythene.

Ans. Polythene < Buna-S < Nylon-66

Nylon-66 Condensation polymer

Buna-S Addition polymer

Polythene Addition polymer

Q.9. What is the function of S in the vulcanization of rubber?

Ans. Sulphur makes the rubber more elastic, more ductile, less plastic and non-sticky

Q.10. Name a polymer which is used for making non-stick utensils.

(Pb. S.E. 2013)

Ans. Teflon.

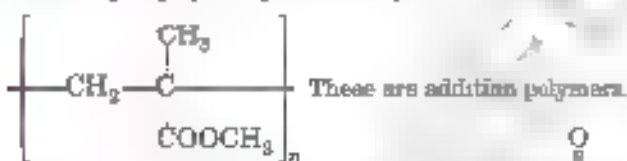
Q.11. Is $+CH_2-CH(C_6H_5)+_n$ a homopolymer or a copolymer? Is it an addition polymer or a condensation polymer?

[N.C.E.R.T.]

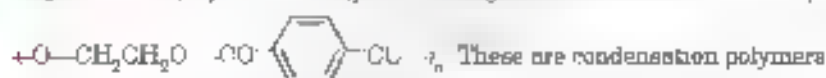
Ans. It is a homopolymer and its monomer is styrene $C_6H_5-CH=CH_2$. Since the monomer contains a double bond, it forms an addition polymer.

Q.12. Explain the difference between polyacrylates and polyesters.

Ans. Polyacrylates are formed from the esters of acrylic acid $-CH_2-CHCOOH$ such as $CH_2=CHCOOR$. For example, polymethyl methacrylate (PMMA)



Polyesters are polymers having ester linkages $\begin{array}{c} \text{O} \\ || \\ \text{C}-\text{O} \end{array}$. For example, terylene.



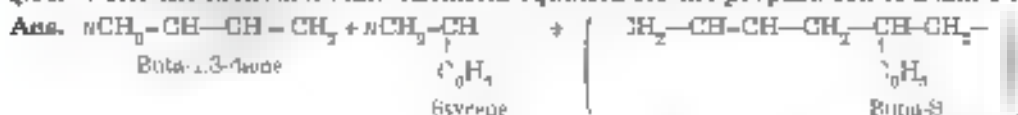
Q.13. Write the structure of a reagent used for initiating a free radical chain reactions. How does it act?

Ans. Tertiary butyl peroxide is used for initiating a free radical chain reaction. It decomposes under mild conditions to form t-butoxide free radical which initiates the reaction



Q.14. Write the monomers and chemical equation for the preparation of Buna-S rubber.

(Pb.S.E. 2005)



Q.15. On the basis of forces between their molecules in a polymer to which class does nylon-66 belong?

(D.S.E. 2005)

Ans. It belongs to the class of fibres

Q.16. Arrange the following polymers in the increasing order of tensile strength.

Nylon 6, Buna-S, Polythene.

(CBSE Sample Paper 2016)

Ans. Buna-S < Polythene < Nylon 6



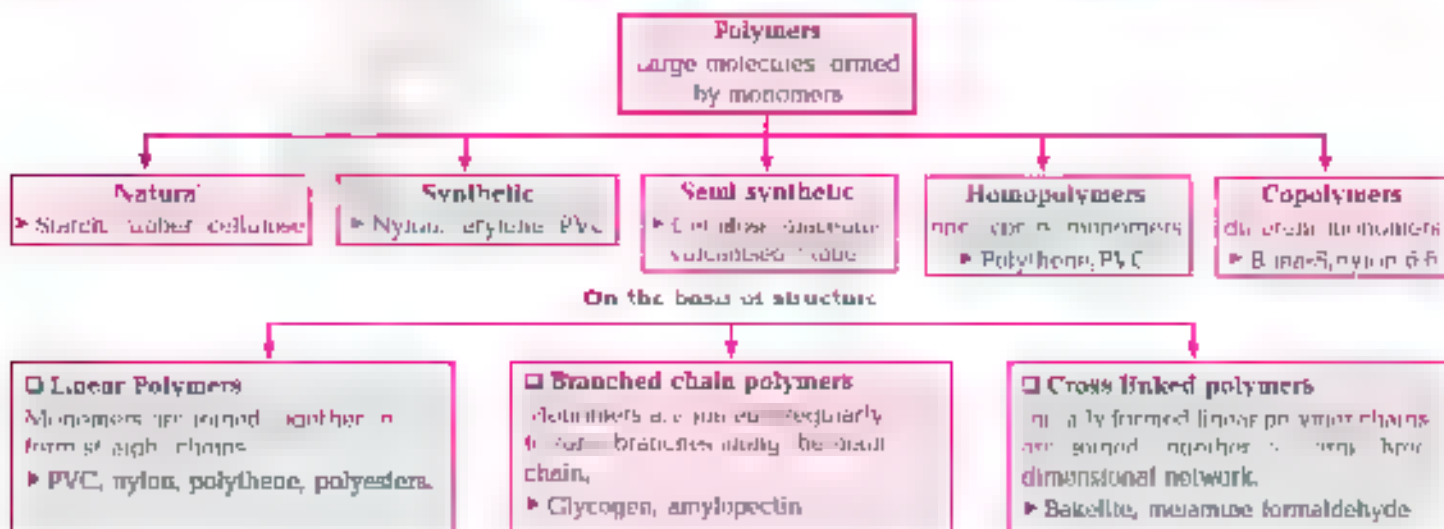
A.I.S.B. 2019

Ans. Homopolymer

Key Terms & Laws

- Polymers** are high molecular mass substances whose molecules consist of repeating units of monomers.
- Homopolymers.** Polymers whose repeating structural unit is derived only from one type of monomer units e.g. polythene, PVC, polypropylene, neoprene, nylon-6.
- Copolymers.** The polymers whose repeating structural unit is derived from two or more monomer units e.g. Nylon-66, Buna-S, bakelite, polyester.
 - ⇒ **Addition polymers.** The polymers formed by direct addition of a large number of monomers are called **addition polymers**.
 - ⇒ **Condensation polymers.** The polymers formed by the condensation of two or more than two monomers by the loss of H_2O , HCl etc.
- Natural polymers.** The polymers obtained from nature plants and animals e.g. starch, cellulose, natural rubber, proteins, etc.
- Synthetic polymers.** The polymers which are prepared by man in laboratories e.g. polyethylene, nylon, arlon, acrylene, teflon, PVC, etc.
- Semisynthetic polymers.** The polymers which are derived from naturally occurring polymers by chemical modifications e.g., cellulose acetate, cellulose nitrate, etc.
- Elastomers.** The polymers in which the intermolecular forces between polymer chains are weakest and have weak character.
- Fibres.** The polymers which have strong intermolecular forces between polymer chains.
- Thermoplastics.** The polymers in which intermolecular forces are intermediate between those of elastomers and fibres. In these polymers, there is cross-linking between the chains.
- Thermosetting polymers.** Low molecular mass semifluid substances which when heated in a mould undergo change in chemical composition to give a hard, infusible and insoluble mass.
- Vulcanisation.** It is a process of treating rubber with 3-5% sulphur to increase its properties such as tensile strength, elasticity and resistance to abrasion.

QUICK CHAPTER ROUND UP



On the basis of intermolecular forces

Q Elastomers

Rubber like solids with elastic properties having weakest intermolecular forces.

► Buna-S, Buna-N, Neoprene

Q Fibres

Thread forming solids possessing high tensile strength and high modulus. These have strong intermolecular forces like hydrogen bonds

► Nylon 6,6; acrylenc

Q Thermoplastics

Have intermolecular forces between those of elastomers and fibres. Hard at room temperature, becomes soft and viscous on heating.

► Polythene, polystyrene, etc.

Q Thermosetting

Cross linked and heavily branched which on heating undergo permanent change by extensive cross linking in moulds

► bakelite, urea-formaldehyde

On the basis of mode of synthesis

Addition polymers

Formed by addition of monomers without elimination of water

► Buna-S, polyethylene

Condensation polymers

Formed by combination of monomers with elimination of water, alcohol, CO_2 , etc.

► Nylon 6, 6, bakelite

• In terms of intermolecular forces

Thermosetting > Thermoplastic > Fibres > Elastomers

Natural rubber is a polymer of isoprene. Zonothylene is addition polymer of isoprene having cross link chain about the double bond.



NCERT FILE

Solved



NCERT

In-text Questions

Q.1. What are polymers?

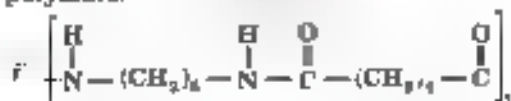
Ans. Polymers are high molecular mass substances formed by the combination of a large number of simple molecules. They are also called macromolecules. For example, polythene, bakelite, etc.

Q.2. How are polymers classified on the basis of structure of polymers?

Ans. On the basis of structure of polymers, these are classified as

- Linear polymers e.g., polythene, nylon, polyvinyl chloride etc.
 - Branched chain polymers e.g., low density polythene, glycogen.
 - Cross linked polymers e.g., bakelite, melamine, etc.
- For details refer Text Page 3-51.

Q.3. Write the names of monomers of the following polymers.



Ans. Monomers of polymers

- Hexamethylene diamine and adipic acid
- Caprolactam
- Tetrafluoroethene

Q.4. Classify the following as addition and condensation polymers:

Terylene, bakelite, polyvinyl chloride, polythene

Ans. Terylene : Condensation polymer
 Bakelite : Condensation polymer
 Polyvinyl chloride : Addition polymer
 Polythene : Addition polymer

Q.5. Explain the differences between Buna-N and Buna-S.

Ans. Buna-N is a copolymer of buta-1,3-diene and acrylonitrile. Buna-S is a copolymer of buta-1,3-diene and styrene.

Q.6. Arrange the following polymers in increasing order of their intermolecular forces:

- Nylon-6, 6, Buna-S, Polythene
- Nylon-6, Neoprene, Polyvinyl chloride

Ans. (i) Buna-S, Polythene, Nylon 6, 6
 (ii) Neoprene, Polyvinyl chloride, Nylon-6



NCERT

Textbook Exercises

Q.1. Explain the terms polymer and monomer.

Ans. Polymer is a high molecular mass macromolecule formed by the combination of a large number of simple molecules. Monomer is a simple molecule capable of undergoing polymerisation to form polymers.

For example, polythene is a polymer and its simple molecule ethene is a monomer



Q.2. What are natural and synthetic polymers? Give two examples of each type.

Ans. Natural polymers are high molecular mass macromolecules obtained from natural sources (plants and animals). For example,

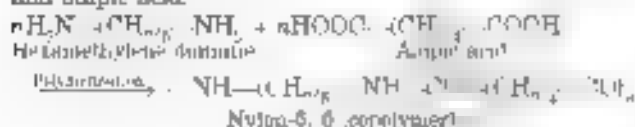
(i) Proteins (ii) Nucleic acids

Synthetic polymers are man made high molecular mass macromolecules which are prepared in laboratories. For example

(i) Polythene (ii) Nylon

Q.3. Distinguish between the terms homopolymer and copolymer and given an example of each.

Ans. Homopolymer is a high molecular mass macromolecule (polymer) which is formed from one type of monomers. For example, polythene is a homopolymer because it is formed from ethene monomer. Copolymer is a high molecular mass macromolecule or polymer which is formed from two or more different monomers. For example, nylon 6, 6 is a copolymer formed from hexamethylene diamine and adipic acid.



Q.4. How do you explain the functionality of a monomer?

Ans. Functionality is the number of bonding sites in a monomer.

Q.5. Define the term polymerisation.

Ans. Polymerisation is a process of formation of high molecular mass polymer from one or more monomers by linking together of repeating structural units with covalent bonds.

Q.6. Is $(\text{NH}-\text{CHR}-\text{CO})_n$ a homopolymer or copolymer?

Ans. Refer Solved Example 1 (Page 8).

Q.7. In which classes, the polymers are classified on the basis of molecular forces?

Ans. On the basis of molecular forces present between the chains of various polymers, these are classified as

- (i) Elastomers e.g., natural rubber, buna-S
- (ii) Fibres e.g., dacron, nylon-6, 6
- (iii) Thermoplastics e.g., polythene, teflon
- (iv) Thermosetting e.g., bakelite, melamine. For details refer Text (Page 4).

Q.8. How can you differentiate between addition and condensation polymerisation?

Ans. In addition polymerisation, the molecules of same or different monomers combine to form a large polymer without the elimination of some other molecules.

In condensation polymerisation, the molecules of two or more bifunctional monomers undergo a series of condensation reactions with the elimination of simple molecules (water, ammonia, alcohol, etc.). For details refer Text (Page 6).

Q.9. Explain the term copolymerisation and give two examples.

Ans. Copolymerisation is a process in which two or more monomers combine to form a polymer. The copolymers contain a multiple units of each monomer in the chain. Examples: (i) 1, 3-butadiene and acrylonitrile

(ii) 1, 3-butadiene and styrene

Q.10. Write the free radical mechanism for the polymerisation of ethene.

Ans. Refer Text (Page 8).

Q.11. Define thermoplastics and thermosetting polymers with two examples of each.

Ans. Thermoplastics are the polymers which can be easily softened repeatedly on heating and hardened on cooling. Therefore, it can be used again and again. For example

(i) Polythene (ii) Polyvinyl chloride

Thermosetting polymers are those which undergo permanent change on heating. They become hard and infusible on heating and cannot be softened again. For example,

(i) Bakelite (ii) Melamine formaldehyde.

Q.12. Write the monomers used for getting the following polymers:

- (i) Polyvinyl chloride
- (ii) Teflon
- (iii) Bakelite

Ans. (i) Polyvinyl chloride $\text{CH}_2=\text{CHCl}$ vinyl chloride

(ii) Teflon $\text{CF}_3=\text{CF}_2$ tetrafluoroethene

(iii) Bakelite $\text{C}_6\text{H}_5\text{OH}$ (phenol) and HCHO (formaldehyde)

Q.13. Write the name and structure of one of the common initiators used in free radical addition polymerisation.

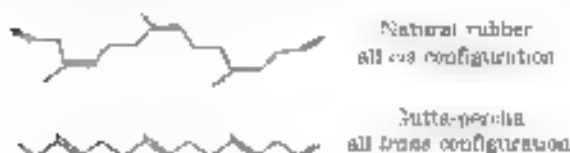


Q.14. How does the presence of double bonds in rubber molecules influence their structure and reactivity?

Ans. Natural rubber is a linear cis-1, 4-polyisoprene in which double bonds are present between C_2 and C_3 of isoprene units. The cis configuration about double bonds does not allow the chains to come closer for effective intermolecular

attraction due to weak intermolecular attractions. Therefore, the natural rubber has coiled structure and shows elasticity and is non-crystalline.

On the other hand, all *trans* configurations occur in gutta-percha which is *trans* polyisoprene. These zig-zag chains pack more closely in gutta-percha and hence it is highly crystalline and non-elastic and is more hard and brittle than rubber.



Q.16. Discuss the main purpose of vulcanization of rubber.

Ans. Refer Text (Page 14)

Q.16. What are the monomeric repeating units of nylon-6 and nylon-66?

Ans. Nylon 6 $[\text{NH}-(\text{CH}_2)_5-\text{CO}]_n$ Caprolactam
Nylon 6, 6 $[\text{NH}-(\text{CH}_2)_6-\text{NH}-\text{CO}-(\text{CH}_2)_4-\text{CO}]_n$
derived from hexamethylene diamine and adipic acid.

Q.17. Write the names and structures of the monomers of the following polymers:

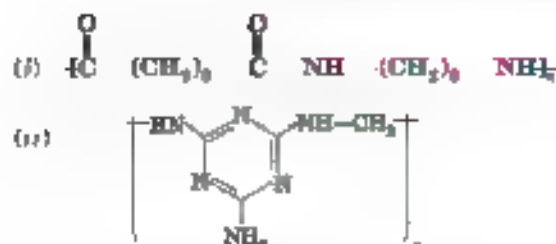
i) Buna-S ii) Buna-N
iii) Dacron iv) Neoprene.

Ans. i) Buna-S 1. 3-Butadiene $\text{H}_2\text{C}=\text{CH}-\text{CH}=\text{CH}_2$
Styrene $\text{C}_6\text{H}_5\text{CH}=\text{CH}_2$
ii) Buna-N 1. 3-Butadiene $\text{H}_2\text{C}=\text{CH}-\text{CH}=\text{CH}_2$
Acrylonitrile $\text{CH}_2=\text{CH}-\text{CN}$
iii) Dacron Ethylene glycol CH_2-CH_2
 $\text{OH} \quad \text{OH}$

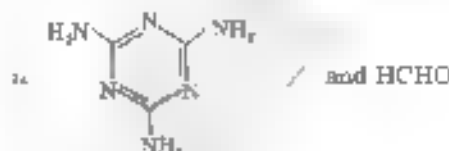


iv) Neoprene Chloroprene $\text{CH}_2=\text{C}(\text{CH}_3)-\text{CH}=\text{CH}_2$

Q.18. Identify the monomer in the following polymer structure:

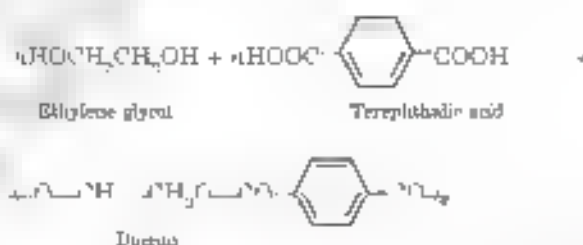


Ans. (i) $\text{HOOC}-(\text{CH}_2)_8-\text{COOH}$ Decanoic acid
 $\text{NH}_2-(\text{CH}_2)_6-\text{NH}_2$ Hexamethylenediamine



Q.19. How is dacron obtained from ethylene glycol and terephthalic acid?

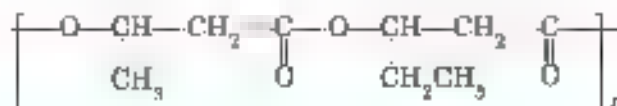
Ans. Dacron is obtained by the polymerisation of ethylene glycol and terephthalic acid.



Q.20. What is a biodegradable polymer? Give an example of a biodegradable aliphatic polyester.

Ans. The polymers which are degraded by micro-organisms within a suitable period so that the polymers and their degraded products do not cause any serious effects on the environment are called biodegradable polymers. For example,

Poly β -hydroxy butyrate-co- β -hydroxyvalerate (PHBV)



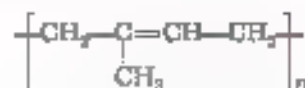
NCERT

Exemplar Problems

Subjective Questions

of the product of this treatment.

Ans. $\text{CH}_2=\text{C}(\text{CH}_3)-\text{CH}=\text{CH}_2$



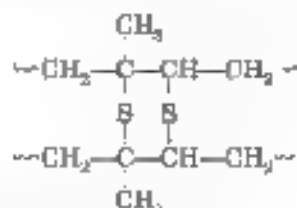
Polyisoprene
natural rubber

Objective Questions from Exemplar Problems are given in Companion Book, page 48

Short Answer Type Questions

1. A natural linear polymer of 2-methyl 1,3-butadiene becomes hard on treatment with sulphur between 373 to 415 K and S-S bonds are formed between chains. Write the structure

When it is heated with S at 373–413 K, it results into S-S links forming



This is called vulcanisation of rubber

2. Identify the type of polymer.



Ann. Homo polymer

8. Identify the type of polymer.



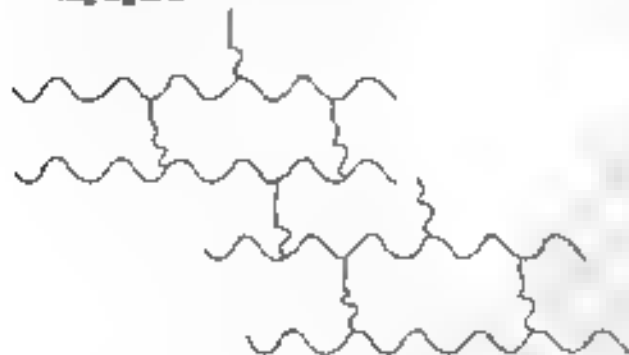
Ann. Coulter

4. Out of chain growth polymerisation and step growth polymerisation, in which type will you place the following?



Anal. Calcd. for $C_{10}H_{12}O_2$: C, 77.7%; H, 7.7%. Found: C, 77.5%; H, 7.5%.

5. Identify the type of polymer given in the following figure.



Ans. Cross-linked polymerization

6. Identify the polymer given below:



Ann. Polyisoprene or natural rubber

7. Why are rubbers called elastomers?

Ans. When force is applied, rubbers are stretched and then regain original state after the force is removed. Therefore, these are called elastomers.

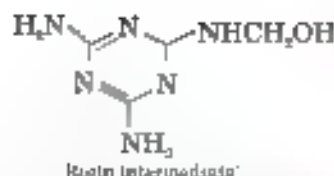
8. Can enzyme be called a polymer?

Ans. Enzymes are biocatalysts which are proteins and are thus polymers.

9. Can nucleic acids, proteins and starch be considered as step growth polymers?

Ans. Yes, step growth polymers are condensation polymers and they are formed by the loss of simple molecule like water leading to the formation of high molecular mass polymers.

10. How is the following resin intermediate prepared and which polymer is formed by this monomer unit?



Knoten unter Verwendung

Ans. The starting materials for this intermediate are melamine and formaldehyde. Its polymerisation gives melamine polymer.

1. To have practical applications why are cross links required in rubber?

Ans. The cross-links make the rubber hard, tough with greater tensile strength. The vulcanised rubber has excellent elasticity, low water absorption tendency, resistance to oxidation and organic solvents.

12. Why does *trans*-polyisoprene possess elastic property?

Ans. In cis-configuration of polyisoprene, there are weak van der Waals forces and therefore, it is elastic.

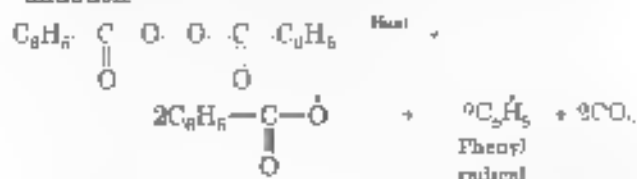
13. What is the structural difference between HDP and LDP? How does the structure account for different behaviour and nature, hence the use of a polymer?

Ans. LDP consists of highly branched chain molecules. Due to branching, the molecules do not pack well and therefore, it has low density (0.93 g cm^{-3}) and low melting point. LDP is transparent of moderate tensile strength and high toughness. It is chemically inert.

HDP consists of linear chains and therefore the molecules can closely pack in space. Therefore it has high density (0.97 g cm^{-3}) and high melting point. It is quite hard, tougher and has greater tensile strength than LDP.

4. What is the role of benzoyl peroxide in addition polymerisation of alkenes? Explain its mode of action with the help of an example.

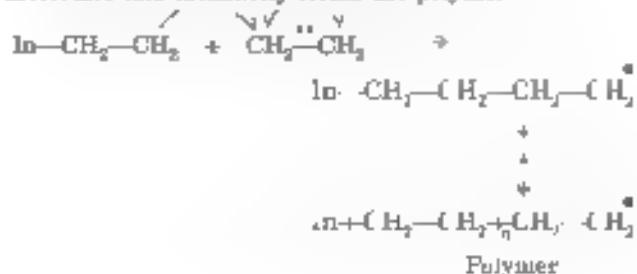
Ans. Benzoyl peroxide acts as an initiator in free radical addition polymerisation of alkenes by providing chain initiation.



The radical formed adds to the carbon-carbon double bond of an alkene molecule to form a new free radical;



The new free radical adds to a double bond of monomer to form a larger free radical which adds to another alkene molecules and ultimately forms the polymer



15. Which factor imparts crystalline nature to a polymer like nylon?

Ans. Strong intermolecular forces such as hydrogen bonding leads to close packing of chains. This imparts crystalline nature to polymer such as nylon.

16. Name the polymers used in laminated sheets and give the name of monomeric units involved in its formation.

Ans. The polymer is urea-formaldehyde resin.

Monomers	Urea	NH_2CONH_2
	Formaldehyde	HCHO



Quick

MEMORY TEST



A. Say True or False

1. Caprolactam is a monomer of nylon 6, 11.
2. Buna-S is an example of elastomers.
3. Bakelite is an example of thermoplastic.
4. PDI is used to determine the homogeneity of polymers.
5. Ethylene glycol and phthalic acid are monomers of glyptal.
6. Polythene is a copolymer.
7. PVC, dacron, bakelite and polystyrene are examples of synthetic polymers.
8. Nylon has the weakest intermolecular forces of attraction.
9. Teflon is used for making nonstick utensils.
10. Bakelite, melamine formaldehyde and buna-S are examples of thermosetting polymers.

B. Complete the missing links

1. Hexamethylenediamine and adipic acid are monomers of _____.
2. Buna-S is copolymer of _____ and _____.
3. The process of vulcanization was introduced by _____.
4. Nylon 6 is obtained by polymerisation of _____.
5. The polymer used for making non stick utensils is _____.
6. Natural rubber is a polymer of _____.
7. The trade name of polyacrylonitrile is _____.
8. The thermosetting polymer whose one monomer is phthalic acid is _____.
9. Terylene is a polymer of _____ and _____.

17. Which type of biomolecules have some structural similarity with synthetic polyamides? What is this similarity?

Ans. Proteins. Polyamides and proteins contain amide linkages.

18. Why should the monomers used in addition polymerisation through free radical pathway be very pure?

Ans. Pure monomers are required because even the traces of impurities may act as initiators which leads to the formation of polymers of small chain lengths.

10. Formaldehyde is one of the monomers of _____ and _____.

11. The monomers of nylon-2-nylon-6 are _____ and _____.

12. PHBV is biodegradable polymer and its monomers are _____ and _____.

13. In Buna-S, S stands for _____.

14. Di-n-butylphthalate is a _____.

15. Neoprene is a polymer of _____.

C. Choose the correct alternative

1. Dextran is a polyamide/polyester polymer which is widely used as a suture.
2. In nylon, intermolecular forces of attraction are hydrogen bonding/dipole-dipole interactions.
3. PHBV is a biodegradable/non biodegradable polymer.
4. Buna-S is a homopolymeric/copolymer.
5. The monomers of bakelite are formaldehyde and phenol/ethylene glycol.
6. $-\text{NH}-\text{CHR}-\text{CO}-$ is a homopolymeric/copolymer.
7. Nylon-6 is a addition polymer/condensation polymer.
8. Vulcanised rubber is obtained by heating natural rubber with sodium/sulphur.
9. Buna-N and Buna-S are examples of elastomers/thermoplastics.
10. Polythene is thermoplastic / thermosetting polymer.

Answers

QUICK

MEMORY TEST



A. Say True or False

1. False 2. True
3. False. Bakelite is thermosetting polymer
4. True. 5. True
6. False 7. True
8. False. It has strongest forces of attraction.
9. True 10. False

B. Complete the missing links

1. nylon 6 6
2. buta-1,3-diene, styrene
3. Charles Goodyear
4. caprolactam
5. teflon
6. isoprene

7. orlon or acrilan
8. bakel or
9. ethylene glycol terephthalic acid
10. bakelite, melamine formaldehyde resin
11. glycine, amino caproic acid
12. 3-hydroxybutanoic acid, 3-hydroxypentanoic acid
13. styrene
14. plasticizer
15. chloroprene

C. Choose the correct alternative

- | | |
|------------------|---------------------|
| 1. polyester | 2. hydrogen bonding |
| 3. biodegradable | 4. copolymer |
| 5. phenol | 6. homopolymer |
| 7. condensation | 8. sulphur |
| 9. elastomers | 10. thermoplastic |

HOTS

Higher Order Thinking Skills & Advanced Level

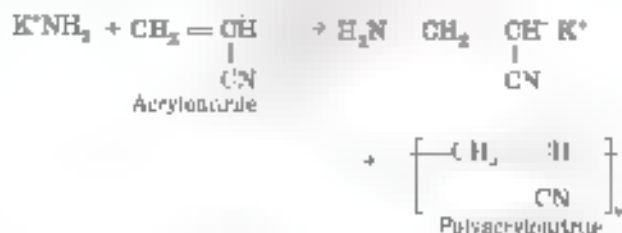
QUESTIONS WITH ANSWERS

Q.1. Why should one always use purest monomer in free radical polymerisation reaction?

Ans. In free radical polymerisation reaction, the impurities can act as chain transfer agent and may combine with the free radical to slow down the reaction or even stop the reaction.

Q.2. Will you prefer to polymerize acrylonitrile under anionic or cationic conditions. Explain.

Ans. Acrylonitrile ($\text{CH}_2 = \text{CH}-\text{CN}$) contains an electron withdrawing ($-\text{CN}$) group which can stabilise the carbanion intermediate. Since in anionic polymerization, carbanion intermediates are produced, therefore, polymerization of acrylonitrile must be carried out under anionic conditions.

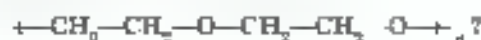


Q.3. Could a co-polymer be formed in both addition and condensation or not? Explain with examples.

Ans. Co-polymers can be formed both by addition and condensation polymerization. For example, styrene

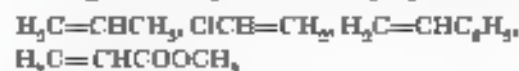
butadiene rubber is a co-polymer which is obtained by addition polymerization while nylon-66 is a copolymer obtained by condensation polymerization.

Q.4. What is the monomer of



Ans. Monomer is ethylene oxide

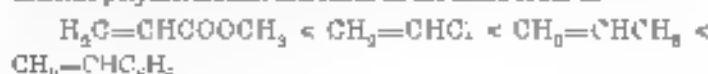
Q.5. Arrange the following alkenes towards order of increasing reactivity in cationic polymerization



Ans. Reactivity of an alkene towards cationic polymerization increases as the stability of the intermediate carbocation formed increases. Since the stability of the carbocation increases in the order



therefore, the reactivity of the corresponding alkenes towards cationic polymerization increases in the same order as



Q.6. Arrange the following alkenes in order of increasing reactivity towards anionic polymerization.



Ans. Reactivity of alkene towards anionic polymerization increases as the stability of the intermediate carbanion increases. The stability of the carbanion increases as

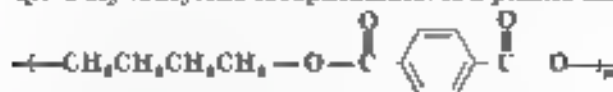


(where B is any base or a nucleophile).

Therefore, the reactivity of the corresponding alkene towards anionic polymerization increases in the same order



Q.7. Poly (butylene terephthalate) is a plastic material used in automotive ignition systems and has the formula:



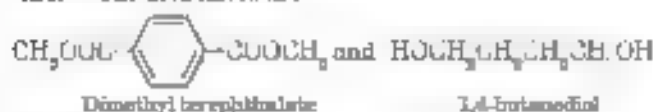
(i) Suggest the monomers which might be used to synthesise this polymer.

(ii) What type of polymer is it ?

(iii) Is this an addition polymer or condensation polymer ?

(iv) Write the reaction.

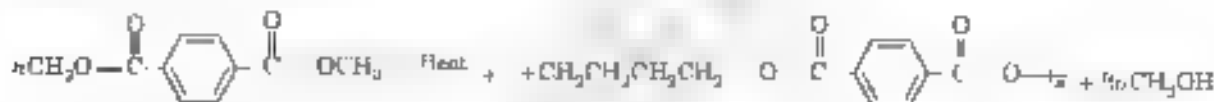
Ans. i. The monomers are



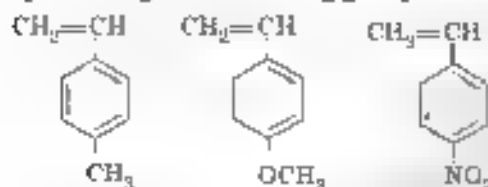
ii. It is a polyester

iii. Condensation polymer

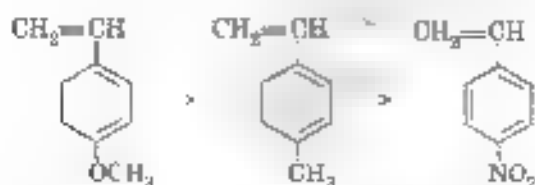
iv. $n\text{HOCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{OH} +$



Q.8. Arrange the following groups of monomers in order of decreasing ability to undergo cationic polymerization:



Ans. Reactivity of an alkene towards cationic polymerization increases with increase in stability of the intermediate carbocation. Therefore, decreasing order of cationic polymerization is



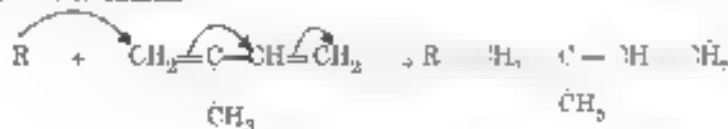
Q.9. Propose a free radical mechanism of polymerization of isoprene.

Ans. Isoprene is a monomer of natural rubber. The free radical mechanism may be depicted as

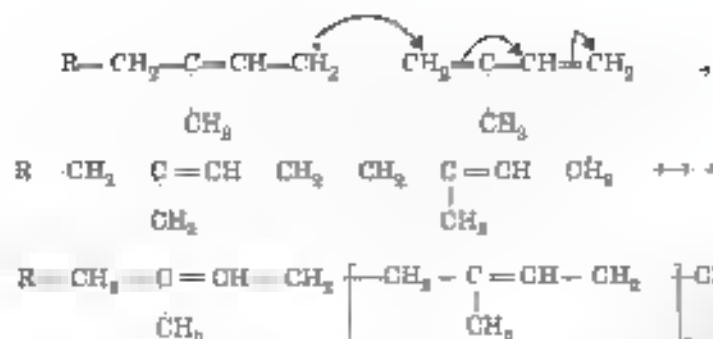
Chain initiation

Initiator

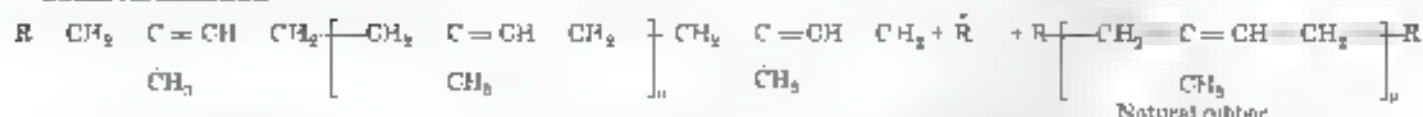
$\rightarrow \text{R}^\bullet$ radical



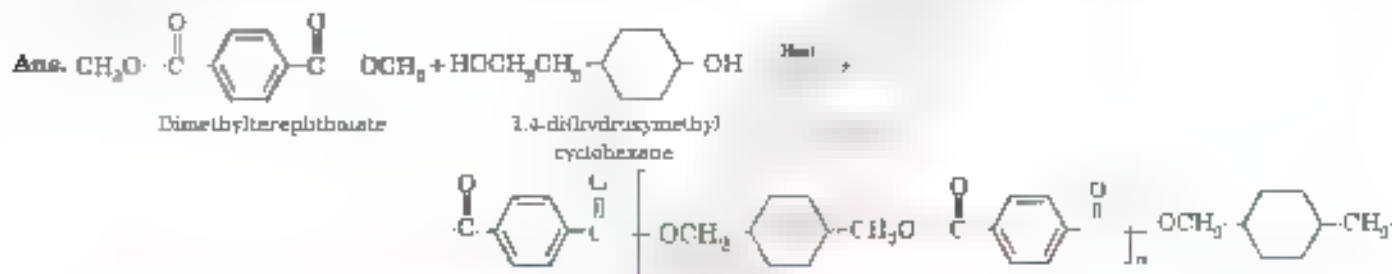
Chain propagation



Chain termination



Q.10. Kodel polyester is formed by trans-esterification of dimethyl terephthalate with 1,4-di (hydroxymethyl) cyclohexane. Write its reaction.



Revision Exercises

Very Short Answer Questions

carrying mark

- Write the IUPAC name of the monomer of natural rubber. *Hr S.B. 2017*
- Explain the term addition-polymerisation with an example. *Hr S.B. 2017*
- What are plasticizers? Give one example. *Pb.S.B. 2006*
- Write the name of one copolymer. *(Pb.S.B. 2011)*
- What is the name of polymer which is also known as urea? *H.P.S.B. 2011*
- What are biodegradable polymers? Give example. *D.S.B. 2011 Hr S.B. 2014, 2017*
- In nylon 6,6, what does the designation '6, 6' mean? *D.S.B. 2011*
- What are the monomeric units of nylon-6, 6? *H.P.S.B. 2011 Pb.S.B. 2012*
- Write the monomers of bakelite. *(Pb.S.B. 2012, 2013)*
- Define the term homopolymerisation giving an example. *(D.S.B. 2012)*
- Write the monomers of dacron. *(H.P.S.B. 2013)*
- Explain the term co-polymerisation with example. *Hr S.B. 2014, 2017*
- What are non-biodegradable polymers? Give example. *J.K.S.B. 2013*

14. Write two examples of synthetic polymers.

*(Tarakhand S.B. 2014)*15. Write the name and structure of the monomers of Buna-S. *Pb.S.B. 2014*16. Write the name and structure of the monomers of Buna-N. *Pb.S.B. 2014*17. Write the name and the structure of monomer of polystyrene. *Pb.S.B. 2016*18. Write the name and the structure of monomer of polyvinyl chloride. *Pb.S.B. 2016*19. What is the cross linked polymer obtained by the polymerisation of phenol and formaldehyde? *Kerala S.B. 2018*

CBSE QUESTIONS

20. What is the primary structural feature necessary for a molecule to make it useful in a condensation polymerisation reaction? *(A.I.S.B. 2010)*21. Is $\left[\text{CH}_2-\underset{\text{Cl}}{\text{CH}} \right]$ a homopolymer or a copolymer? *(A.I.S.B. 2013)*22. Give one example of a condensation polymer. *(A.I.S.B. 2013)*

23. Which of the following is a natural polymer?

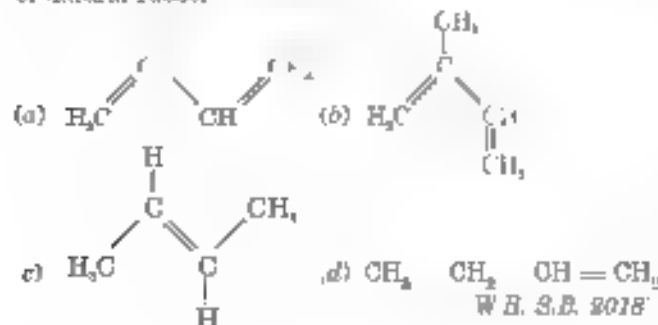
Buna-S, Proteins, PVC *(A.I.S.B. 2014)*24. Based on molecular forces what type of polymer is neoprene? *(A.I.S.B. 2014)*

25. Which of the following is a fibre?

Nylon, Neoprene, PVC *(A.I.S.B. 2014)*

MCQs From State Boards Examinations

25. Polystyrene is a
(a) addition polymer (b) thermoplastic polymer
(c) both a and b (d) none of these
Hr S.B. 2015
27. Cellulose is a
(a) natural polymer (b) semi-synthetic polymer
(c) synthetic polymer (d) none of these
Hr S.B. 2015
28. Buna S is a
(a) addition polymer (b) condensation polymer
(c) both a and b (d) none of these
Hr S.B. 2013
29. Bakelite is a
(a) addition polymer (b) thermoplastic polymer
(c) elastomer polymer (d) thermosetting polymer
Hr S.B. 2013
30. Which of the following is called a polyamide?
(a) Rayon (b) Nylon
(c) Terylene (d) Bakelite
J.K.S.B. 2013
31. Which is a condensation polymer?
(a) PVC (b) Teflon
(c) Bakelite (d) None of these
Hr S.B. 2014
32. Bakelite is a product of the reaction between
(a) Formaldehyde and NaOH
(b) Aniline and Urea
(c) Phenol and Methanol
(d) Phenol and Formaldehyde
J.K.S.B. 2014
33. Vulcanisation makes rubber
(a) more elastic (b) sol soluble in organic solvents
(c) crystalline (d) none of these
H.P.S.B. 2016
34. Neoprene is a polymer of
(a) Chloroprene (b) Isoprene
(c) Styrene (d) Ethene
Hr S.B. 2018
35. The monomer unit of PVC is
(a) vinyl chloride (b) ethylene
(c) chloroprene (d) acrylonitrile
H.P.S.B. 2017
36. Which of the following is not applicable to Nylon-6, 6?
(a) Synthetic polymer (b) fibre
(c) Addition polymer (d) Condensation polymer
37. In the following thermosetting polymer is
(a) Bakelite (b) Polystyrene
(c) Polyester (d) Buna N
(Hr S.B. 2018)
38. Monomer of tetlon is
(a) $\text{CF}_3 = \text{CF}_3$ (b) $\text{CH}_2 = \text{CHCN}$
(c) $\text{CH}_2 = \text{H}_2$ (d) $-\text{H}_2\text{C} = \text{H} - \text{H}_2$
Hr S.B. 2018
39. Which of the following can be considered as the monomer of natural rubber?



Short Answer Questions

carrying 2 or 3 marks

1. Define the following terms and give one example for each
(i) Synthetic polymers (ii) Natural polymers
(iii) Condensation polymers (iv) Thermosetting polymers
(v) Addition polymers
(Hr S.B. 2015)
2. Write the structure of monomer of each of the following polymers
(i) Polyvinyl chloride
(ii) Nylon-6
(D.S.B. 2007)
3. (a) What are copolymers? Give chemical equation for preparation of glyptal.
(b) What are elastomers? Write chemical equation to represent the preparation of Buna-S
(H.P.S.B. 2008)
4. Write the names and structures of the monomers of the following polymers
(i) Buna-S (ii) Neoprene
(iii) Nylon-6
(D.S.B. 2008, 2017)
5. Draw the structures of the monomers of the following polymers
(i) Teflon (ii) Polyvinyl chloride (PVC)
(iii) Melamine-formaldehyde polymer
(D.S.B. 2008, 2017)
6. (a) How will you prepare polymer dacron? Give its chemical reaction.
(b) Give the common and IUPAC name of the monomer of natural rubber
(H.P.S.B. 2010)
7. (a) How will you prepare polymer PAN, polyacrylonitrile? Give its chemical reaction.
(b) Give the name of the polymer which is used for making non-stick utensils.
(H.P.S.B. 2010)
8. What is the repeating unit in the condensation polymer obtained by combining $\text{HO}_3\text{CCH}_2\text{CH}_2\text{COOH}$ (succinic acid) and $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$ (ethylene diamine)?
(D.S.B. 2010)
9. Differentiate between molecular structures and behaviours of thermoplastic and thermosetting polymers. Give one example of each type.
(A.I.S.B. 2010)
10. Mention two important uses of each of the following
(i) Bakelite (ii) Nylon-6
(D.S.B. 2011)
11. Name the subgroups into which polymers are classified on the basis of magnitude of intermolecular forces
(D.S.B. 2011)
12. What is vulcanisation of rubber? What are the advantages of vulcanized rubber?
(H.P.S.B. 2012, 2016)
13. What are polymers? What is the difference between homopolymer and co-polymer? Give examples.
(H.P.S.B. 2012, Meghalaya S.B. 2017)
14. (a) Name a polymer which is used as a substitute for wool. What is its monomer unit?
(b) What are natural and synthetic polymers? Give one example of each type.
(c) Discuss the main purpose of vulcanisation of rubber
(Meghalaya S.B. 2018)
15. (i) What is vulcanisation of rubber?
(ii) What is the monomer of natural rubber?
(iii) Define elastomer
(H.P.S.B. 2018)

16. Differentiate between addition and condensation polymerization. Give two examples of each.
(Hr S.B. 2018, 2017; Meghalaya S.B. 2015)
17. a) Name the monomers of bakelite.
b) What is the primary feature necessary for a monomer to make it useful in a condensation polymerization reaction?
c) What is meant by copolymerization? Give one example of a copolymer. (Assam S.B. 2013)
18. Write the names and structures of the monomers of the following polymers:
i) Buna-N ii) Neoprene
iii) Dacron (D.S.B. 2013, 2017)
19. a) How is Nylon-6, 6 obtained? Give one of its uses.
b) What are biodegradable and non-biodegradable polymers? Give one example each. (Nagaland S.B. 2018)
20. What are addition polymers? Write the chemical equation for the preparation of synthetic rubber. (Mizoram S.B. 2014)
21. a) Give the common and IUPAC names of the monomer of natural rubber.
b) How is high density polythene obtained? What structural difference it has from low density polythene?
c) Name a copolymer which is used for making non-breakable plastic crockery?
d) Write the names and give the structures of the monomers of Nylon-6,6. (Meghalaya S.B. 2018)
22. a) Write any two differences between step growth polymerisation and chain growth polymerisation.
b) What are the monomers of the following:
i) Neoprene ii) Nylon-6 (Kerala S.B. 2014)
23. a) What are copolymers? Give chemical equation for the preparation of glyptal. (H.B.S.B. 2015)
b) What are the monomers of bakelite? (H.B.S.B. 2015)
24. Explain the method to prepare nylon-6 and nylon-6,6 polymers. (H.S.B. 2015)
25. Polymers are macromolecules formed by the union of monomers.
a) Name natural polymers and synthetic polymers.
b) Distinguish between thermoplastic and thermosetting polymers with example. (Kerala S.B. 2015)
26. What is vulcanisation? Give two points of differences between natural rubber and vulcanised rubber. (Mizoram S.B. 2015)
27. a) What are the monomer units of the polymer nylon-2-nylon-6? Is this polymer biodegradable?
b) What are elastomers? Give one example. (Meghalaya S.B. 2013)
28. a) What is Buna-S? Give two uses of it.
Or
b) What are biodegradable polymers? Give two examples. (Nagaland S.B. 2015)
29. a) What are polymers?
b) Name the monomers of polythene, teflon and nylon-6,6.
Or
a) What is vulcanisation of rubber?
b) What is the role of sulphur in vulcanisation of rubber? (Assam S.B. 2015)
30. a) Write difference between thermoplastic and thermosetting polymers. (Hr S.B. 2018, H.P. S.B. 2018)
b) Explain the difference between polymer Nylon-6,6 and Nylon-6. (Hr S.B. 2018)
c) Differentiate between the monomers of Buna-N and Buna-S. (Hr S.B. 2018)
31. Write the names and structures of the monomers of the following polymers.
i) Nylon 6,6 ii) PHBV
iii) Neoprene (D.S.B. 2015)
32. a) Give synthesis of Buna-S.
i) What are fibres?
ii) Give synthesis of Nylon-6, 6. (H.P.S.B. 2018)
33. a) Write any three points of differences between addition and condensation polymers. (Mizoram S.B. 2018)
b) Explain biodegradable polymers. (H.P.S.B. 2018)
34. How is nylon-66 obtained? (Nagaland S.B. 2016)
35. a) Write the name and structure of monomers of i) Bakelite ii) Polythene.
b) What are biodegradable polymers?
Or
a) Give one example each of
i) Addition polymers
ii) Condensation polymers
b) Why is rubber vulcanised? (Tripura S.B. 2016)
36. a) Classify the following polymers into elastomers and fibres.
Rubber, Nylon-6,6, Buna-S, Terylene.
b) What do you mean by thermosetting polymers? Give one example. (Kerala S.B. 2016)
37. a) Name the monomers of i) Buna-N and ii) SBR.
b) What are low density and high density polyethylenes? (Meghalaya S.B. 2018)
38. a) Explain the preparation of Nylon-6, 6 with equation.
b) What are thermoplastic polymers? Give an example.
c) Write the structure of isoprene (2-methyl-1,3-butadiene). (Karnataka S.B. 2018)
39. Write the monomers used for preparing the following polymers:
i) Glyptal ii) Nylon-6,6 (Hr S.B. 2017)
40. Write down differences between terylene fibres and Buna-S rubber (elastomers). (Ph.S.B. 2017)
41. a) Give one example of addition homopolymer.
b) Mention one use each of LDP and HTP.
c) What is the monomer unit of natural rubber? (Assam S.B. 2017)
42. a) What are addition and condensation polymers? Give an example of each type.
b) Name the polymer which can be used as a substitute for wood.
Or
c) Write the equation for the synthesis of terylene from ethylene glycol and terephthalic acid.
d) Define thermoplastics and thermosetting polymers with an example of each. (Meghalaya S.B. 2017)
43. a) How can Buna-S be prepared? Give one use of it.
Or
b) What is LDPE and HDPE? (Nagaland S.B. 2017)

44. How is bakelite made and what is its major use? Why is bakelite a thermosetting polymer? (Manipal S.B. 2017)
45. Differentiate between thermoplastics and thermosetting plastics. Write one example of each. (Kerala S.B. 2017)
46. (i) Give one example of homopolymer and one example of co-polymer.
(ii) Mention the structural difference between thermoplastic and thermosetting polymer.
(iii) Give one use of high density polythene (HDP). (Assam S.B. 2018)
47. What are biodegradable polymers? Give chemical equation for the preparation of any one biodegradable polymer. (Pb S.B. 2018)

CBSE QUESTIONS

48. Differentiate between condensation and addition polymerisation. Give one example each of the resulting polymers. (A.S.B. 2002, 2010, Pb S.B. 2017)
49. Differentiate between thermoplastics and thermosetting polymers. Give one example of each. (A.I.S.B. 2013, Hr S.B. 2010)
50. Define thermoplastic and thermosetting polymer. Give one example of each.
Or
What is a biodegradable polymer? Give an example of a biodegradable aliphatic polyester. (A.I.S.B. 2017)
51. Write the names and structures of the monomers of the following polymers:
(i) Nylon-6 (ii) Neolac (iii) Buna-N (A.I.S.B. 2015)

52. (i) What is the role of *t*-butyl peroxide in the polymerisation of ethene?
(ii) Identify the monomers in the following polymer:
 $\text{+ NH}-(\text{CH}_2)_6-\text{NH}-\text{CO}-(\text{CH}_2)_4-\text{CO-}_n$
(iii) Arrange the following polymers in the increasing order of their intermolecular forces:
Polystyrene, Terylene, Buna-S
Or
Write the mechanism of free radical polymerisation of ethene. (D.S.B. 2016, A.S.B. 2019)
53. Write the structures of the monomers used for getting the following polymers:
(i) Polyvinyl chloride (PVC)
(ii) Melamine-formaldehyde polymer
(iii) Buna-N (A.I.S.B. 2014, 2015, 2017)
54. Write the structures of the monomers used for getting the following polymers:
(i) Teflon
(ii) Melamine-formaldehyde polymer
(iii) Neoprene (A.I.S.B. 2014, 2015, 2017)
55. Write the structures of the monomers used for getting the following polymers:
(i) Nylon-6,6
(ii) Melamine-formaldehyde polymer
(iii) Buna-S (A.I.S.B. 2014, 2015, 2017)
56. (a) Write one structural difference between low-density polythene and high-density polythene.
(b) What is a biodegradable polymer? Give an example. (A.I.S.B. 2016)

Hints & Answers

for Revision Exercises

Very Short Answer Questions

1. 2-Methylbuta-1,3-diene 5. Polymethylacrylate
8. Hexamethylenediamine and adipic acid
9. Phenol and formaldehyde
11. Ethylene glycol and terephthalic acid
15. Buta-1,3-diene and styrene

16. Buta-1,3-diene and acrylonitrile

19. Bakelite

21. Homopolymer

23. Proteins 24. Elastomer 25. Nylon

26. (b) 27. (a) 28. (a) 29. (d)

30. (b) 31. (c) 32. (d) 33. (a)

34. (a) 35. (a) 36. (d) 37. (a)

38. (a) 39. (b)

Competition File

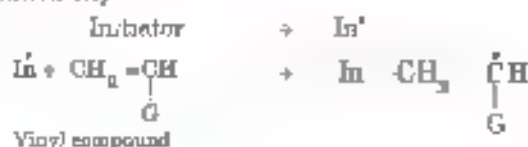
Additional Useful Information and Objective Questions

ADDITIONAL USEFUL INFORMATION

A. Vinyl Polymerisation

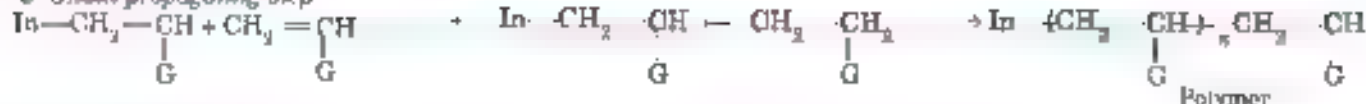
Most of the commercial addition polymers are 'vinyl' polymers obtained from alkenes and their derivatives. $\text{^H} \text{C} = \text{CH} \text{G}$. The polymerisation reaction involves the same steps.

(i) Chain initiation step

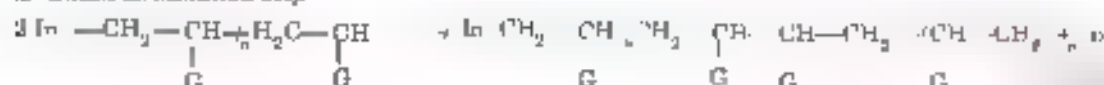


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b Chain propagating step



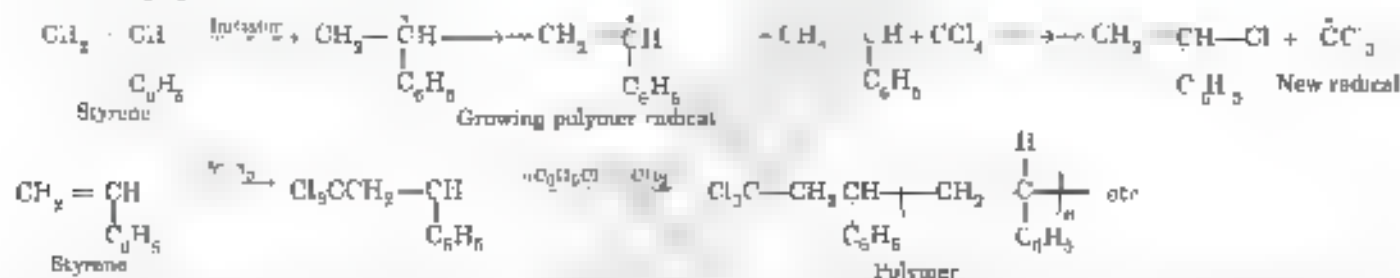
c Chain termination step



Chain transfer agents—Competing reactions in vinyl polymerization

It may be noted that in vinyl polymerisation, various other reactions of free radicals with some other compounds present may compete with the parent chain reactions. For example, the reaction may take place with molecules which can react with growing chain to interrupt the further growth of the original chain. However, the product of such a reaction may initiate its own chain growth. This results in lowering of average molecular mass of the polymer. Such compounds which bring about the termination of the original polymer chain with the simultaneous initiation of another polymer chain are called **chain transfer agents**. The common examples are carbon tetrachloride, carbon tetrabromide, etc. For example, in the presence of carbon tetrachloride, styrene $\text{CH}_2=\underset{\text{C}_6\text{H}_5}{\text{CH}}$ polymerises to

form a polymer of lower average molecular mass which also contains some chlorine. In this polymerisation reaction, growing polystyrene radical which normally would add on a polymer reacts with the chain transfer agent CCl_4 to end the original chain and form a new radical. The latter free radical initiates a new polymerisation chain and forms a new polymer as shown below.



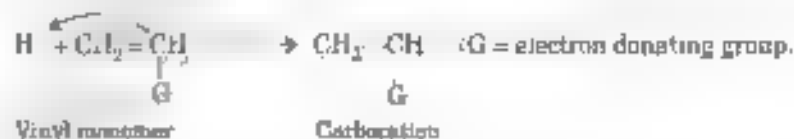
It may be noted that if the chain transfer agent forms a radical which is highly reactive, the chain reaction gets terminated. Therefore, these compounds inhibit further polymerisation and are now called **inhibitors**. Many amines, phenols, quinones, etc. act as inhibitors. Therefore, even traces of certain impurities which can act as chain transfer agents or inhibitors can interfere with the original chain polymerisation reaction. Hence, the monomers should be free from such inhibitors.

B. Cationic Polymerisation

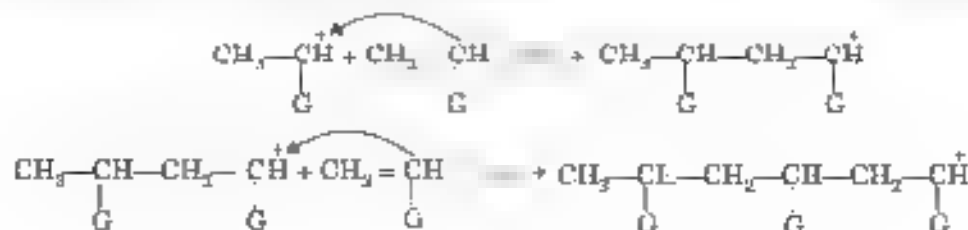
When the initiator is cationic, it adds to the double bond to form a carbocation intermediate for propagating the addition chain process. It is called **cationic addition polymerisation**, it is initiated by acids. The commonly used acids for cationic polymerisation are sulphuric acid H_2SO_4 , HF , BF_3 in the presence of small amount of water.

The chain reaction involves the following steps:

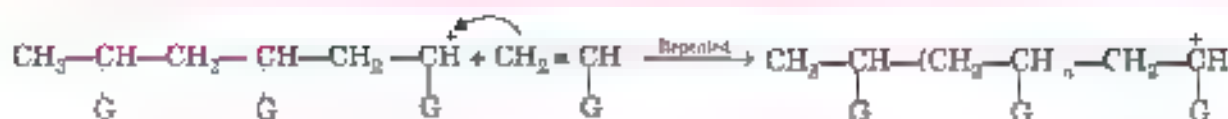
(i) **Chain initiation** The proton adds to the carbon-carbon double bond of alkenes to form a stable carbocation.



(ii) **Chain propagation** The carbocation adds to the carbon-carbon double bond of another monomer molecule to form a new carbocation which can similarly add to another molecule of alkene and so on resulting polymer.



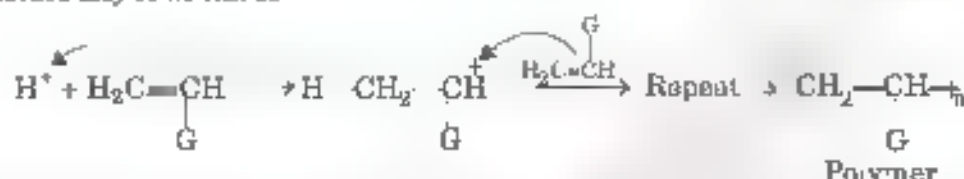
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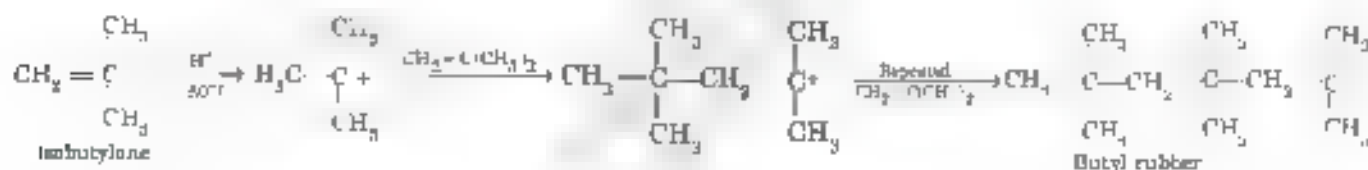
Chain termination. The chain reaction may be terminated by combination of carbocation with negative ion or by loss of a proton



The complete reaction may be written as:

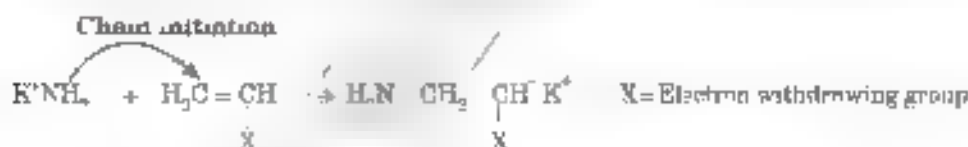


It may be noted that acid catalysed or cation polymerisation is effective only with vinyl monomers which contain an electron donating group (G). These electron donating groups will be able to stabilise the chain carrying carbocation intermediate. Greater the stability of the carbocation intermediate, more facile is the cationic polymerisation. Thus, alkenes containing electron releasing groups are preferably polymerised under cationic conditions though free radical polymerisation may also take place. For example, isobutylene polymerised rapidly under cationic conditions because it has two electron-releasing $-CH_3$ groups that will stabilise the intermediate cation. However, ethylene, vinyl chloride or vinyl cyanide, acrylonitrile, do not undergo polymerisation readily. For example, polymerisation of isobutylene is carried out commercially at -80°C using BF_3 and a small amount of water to generate $\text{BF}_3\text{OH}_2\text{H}^+$ catalyst.

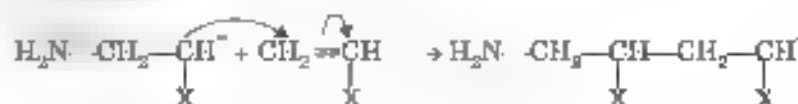


C. Anionic polymerisation

This type of polymerisation is initiated by anions, which may be bases or other nucleophiles. The main chain carrying step is nucleophilic addition of an anion to an unsaturated monomer. It proceeds through the formation of **carbanion**. The initiation may be brought about by reagents such as alkyl anion, or potassium amide K^+NH_2^- . For example,



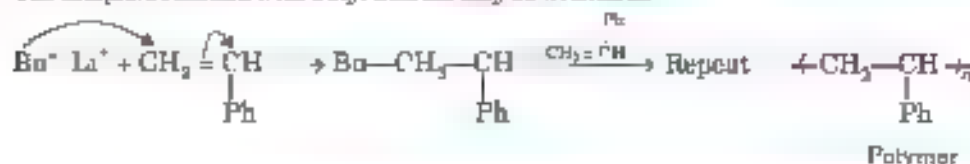
Chain propagation



It may be noted that anion catalysed polymerisation occurs in case of vinyl monomers with electron withdrawing groups (X). Greater the stability of the carbanion intermediate, more facile is the anionic polymerisation. For example, alkenes containing electron withdrawing groups such as, acrylonitrile $\text{CH}_2=\text{CH}(\text{CN})$, methyl methacrylate $\text{H}_2\text{C}=\text{CH}-\text{CH}_3(\text{COOCH}_3)$, styrene $(\text{H}_2\text{C}=\text{CHC}_6\text{H}_5)$, etc. can polymerise anionically.

Competition File

The complete reaction with butyl lithium may be written as



OBJECTIVE TYPE QUESTIONS

Multiple Choice Questions

M. C. Q.

A (TOPICWISE) MULTIPLE CHOICE QUESTIONS with only one correct answer

Polymer and their Classification

- A1.** Which of the following is naturally occurring polymer ?
 (a) Polythene (b) Starch
 (c) Nylon (d) Teflon
- A2.** Which of the following is not an example of addition polymer ?
 (a) Polystyrene (b) Polyethylene
 (c) Polypropylene (d) Terylene
- A3.** Natural rubber is
 (a) neoprene (b) *trans*-polyisoprene
 (c) *cis*-polyisoprene (d) butyl rubber
- A4.** Which of the following is not a biopolymer ?
 (a) Cellulose (b) Proteins
 (c) DNA (d) Nylon-6,6
- A5.** Which of the following is not a step growth polymer ?
 (a) Polybutadiene (b) Nylon-6,6
 (c) Glyptal (d) Terylene
- A6.** Which of the following is a copolymer ?

- (a) $\text{CH}_3 - \text{CH}_2 - \text{C}(\text{COOCH}_3)_2$
 $+ \text{CH}_2 = \text{CH} - \text{C}_6\text{H}_5 \rightarrow \text{C}_6\text{H}_5$
- (b) $+ \text{CH}_2\text{CH} = \text{CH} - \text{CH}_2 - \text{CH} = \text{CH}_2 +$
- (c) $+ \text{CH}_2 - \underset{\text{Cl}}{\text{CH}} -$

- A7.** Polymer formation from monomers starts by
 (a) condensation reaction between monomers
 (b) coordination reaction between monomers
 (c) conversion of monomers to monomer ion by protons
 (d) hydrolysis of monomers
- A8.** Which of the following polymer contains nitrogen ?
 (a) Terylene (b) Nylon-6
 (c) Bakelite (d) Polyvinyl chloride
- A9.** Which of the following is a thermosetting polymer ?
 (a) Teflon (b) PVC
 (c) Glyptal (d) Bakelite
- A10.** Amongst the following, the strongest molecular forces are present in
 (a) fibres (b) elastomers
 (c) thermosetting polymers (d) thermoplastics

Some Important Polymers

- A11.** Neoprene is a polymer of
 (a) chloroprene (b) chloroquin
 (c) propylene (d) isoprene
- A12.** The monomer unit of PVC is
 (a) vinyl chloride (b) ethylene
 (c) chloroprene (d) acrylonitrile
- A13.** Bakelite is the condensation polymer of
 (a) $\text{C}_6\text{H}_5\text{OH}$ and caproic acid
 (b) HCHO and phthalic acid
 (c) $\text{C}_6\text{H}_5\text{OH}$ and HCHO
 (d) HCHO and ethylene glycol
- A14.** Nylon-6, 6 is obtained from
 (a) hexamethylene diamine and adipic acid
 (b) phenol and formaldehyde
 (c) propylene and adipic acid
 (d) adipic acid and phthalic acid

Answers

- A1. (b) A2. (d) A3. (c) A4. (d) A5. (a) A6. (c) A7. (a) A8. (b) A9. (d) A10. (c)
 A11. (a) A12. (a) A13. (c) A14. (a)

Competition File

A15. Buna-S is obtained by the polymerisation of butadiene and

- (a) chloroprene (b) styrene
(c) acrylonitrile (d) adipic acid

A16. Caprolactum polymerises to give

- (a) Nylon-6 (b) Buna-S
(c) Glyptal (d) Teflon

A17. Which of the following fibres is made of polyamides?

- (a) Dacron (b) Orlon
(c) Nylon (d) Rayon

A18. Orlon is a polymer of

- (a) styrene
(b) vinyl chloride
(c) acrylonitrile
(d) butadiene and adipic acid

A19. Which of the following is not a synthetic rubber?

- (a) Neoprene (b) EBR
(c) Thiokol (d) Orlon

A20. Interparticle forces in nylon-66 are

- (a) dipole-dipole interactions
(b) hydrogen bonding
(c) van der Waal's forces
(d) ionic bonds

A21. $F_3C=CF_3$ is a monomer of

- (a) glyptal (b) lexan
(c) orlon (d) buna-S

A22. Terylene is a polymer of ethylene glycol and

- (a) phthalic acid (b) terephthalic acid
(c) adipic acid (d) 1,6-hexanediamine

A23. Which of the following is not a biodegradable polymer?

- (a) PHBV (b) PLA
(c) PMMA (d) PCL

A24. Which of the following statement is not correct regarding vinyl polymerisation?

- (a) It involves free radical addition.
(b) The presence of carbon tetrachloride in styrene polymerisation results in lowering of average molecular mass of the polymer

(c) The presence of benzoquinone increases the polymerisation process

(d) The presence of CCl_4 acts as inhibitor

A25. The monomers of terylene are

- (a) phenol and formaldehyde
(b) ethylene glycol and phthalic acid
(c) adipic acid and hexamethylenediamine
(d) ethylene glycol and terephthalic acid



- (a) Methyl methacrylate (b) Styrene
(c) Propylene (d) Ethene

A27. Which of the following has ester linkage?

- (a) Nylon (b) Bakel
(c) Terylene (d) PVC
(e) Rubber

A28. Which of the following is not correctly matched?

- (a) Neoprene $\left[\begin{array}{c} \text{CH}_3 \\ | \\ \text{CH}_2 - \text{C} = \text{CH} - \text{CH}_2 \end{array} \right]_n$
(b) Nylon-66 $\left[\text{NH} - (\text{CH}_2)_6 - \text{NH} - \text{CO} - (\text{CH}_2)_4 - \text{CO} \right]_n$
(c) Terylene $\left[\text{OCH}_2 - \text{CH}_2 - \text{C}(=\text{O}) - \text{C}_6\text{H}_4 - \text{C}(=\text{O}) \right]_n$
(d) PMMA $\left[\begin{array}{c} \text{CH}_3 \\ | \\ \text{CH}_2 - \text{C} \\ | \\ \text{COOCH}_3 \end{array} \right]_n$

A29. Poly- β -hydroxybutyrate (P3HB) is an example of

- (a) thermoplastics (b) naturally occurring polymer
(c) biodegradable polymer (d) synthetic rubber

A30. A polymer of prop-2-ene is called

- (a) dacron (b) saran
(c) orlon (d) polypropene

- A15. (b) A16. (a) A17. (c) A18. (a) A19. (b) A20. (b) A21. (b) A22. (b) A23. (c) A24. (c)
A25. (d) A26. (a) A27. (c) A28. (c) A29. (c) A30. (d)

Competition File

B (MULTIPLE CHOICE QUESTIONS from competitive Examinations

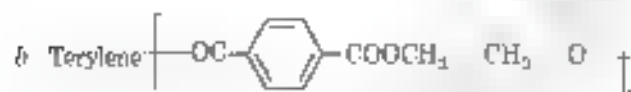
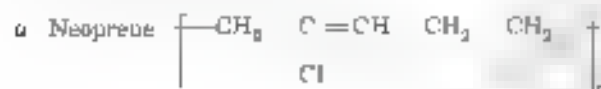
AIPMT & Other State Boards' Medical Entrance

- B1.** $[\text{NH}(\text{CH}_2)_6\text{CONHCO}(\text{CH}_2)_4\text{CO}]_n$ is a
 a. addition polymer (b) thermosetting polymer
 c. homopolymer (d) co-polymer
(C.B.S.E. Med. 2000)

- B2.** Which one of the following polymer is prepared by condensation polymerisation?
 a. Teflon (b) Rubber
 c. Styrene (d) Nylon-6,6
(C.B.S.E. Med. 2007)

- B3.** Which one of the following statements is not true?
 a. Natural rubber has the *trans*-configuration at every double bond
 b. Buna-S is a copolymer of butadiene and styrene
 c. Natural rubber is a 1,4-polymer of isoprene
 d. In vulcanisation the formation of sulphur bridges between different chains make rubber harder and stronger
(C.B.S.E. PMT 2008)

- B4.** Structure of some common polymers are given. Which one is not correctly presented?

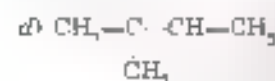


- B5.** Which of the following statements is false?
 a. Artificial silk is derived from cellulose.
 b. Nylon-66 is an example of elastomer
 c. The repeat unit in natural rubber is isoprene
 d. Both starch and cellulose are polymers of glucose
(A.P.M.T. 2012)

- B6.** Nylon is an example of
 a. Polyamide (b) Polythene
 c. Polyester (d) Polysaccharide

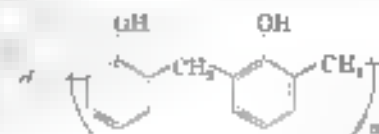
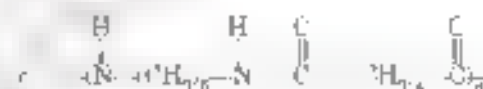
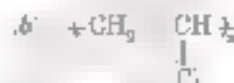
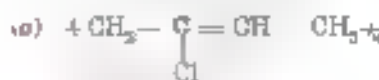
NEET 2013

- B7.** Which is the monomer of neoprene in the following?



(NEET 2013)

- B8.** Which one of the following is an example of thermosetting polymer?



(AIPMT 2014)

- B9.** Which of the following organic compounds polymerizes to form the polyester decron?



(AIPMT 2014)

- B10.** Caprolactam is used for the manufacture of



- B11.** Biodegradable polymer which can be produced from glycine and aminocaproic acid is



- B12.** Natural rubber has

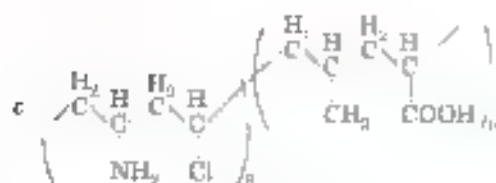


NEET 2010

- B1. d B2. d B3. a B4. a B5. b B6. a B7. a B8. d B9. c B10. c
 B11. c B12. c

Competition File

B13. Which one of the following structures represents nylon 6,6 polymer?



B14. Regarding cross-linked or network polymers, which of the following statement is incorrect?

- (a) They contain covalent bonds between various linear polymer chains
- (b) They are formed from bi- and tri-functional monomers
- (c) Examples are bakelite and melamine
- (d) They contain strong covalent bonds in their polymer chains

B15. Which of the following is not correct regarding terylene?

- (a) Step-growth polymer
- (b) Synthetic fibre
- (c) Condensation polymer (d) also called dacron
- (e) Thermosetting plastic

B16. Plexiglass is a commercial name of

- a. glyptal
- b. polyacrylonitrile
- c. polymethyl methacrylate
- d. polyethylacrylate

B17. The polymer used in orthopaedic devices and in controlled drug release is

- (a) Orion
- (b) PTFE
- (c) SBR
- (d) PHBV
- (e) PVC

B18. Which of the following statement is not correct?

- a. Caprolactam is the monomer of nylon-6
- b. Terylene is a polyester polymer
- c. Phenol formaldehyde resin is known as bakelite
- d. The monomer of natural rubber is butadiene.

DPMT 2010.

B19. Which one of the following is an example of biodegradable polyester?

- (a) PHBV
- (b) PET
- (c) Nylon 6
- (d) Bakelite
- (e) Glyptal

Kerala P.M.T. 2014

B20. The polymer used in the manufacture of squeeze bottles is

- (a) polystyrene
- (b) teflon
- (c) polypropene
- (d) high density polythene
- (e) low density polythene.

Kerala P.M.T. 2015

JEE (Main) & Other State Boards' Engineering Entrance

B21. Which of the following is a polyamide?

- (a) Teflon
- (b) Nylon-6,6
- (c) Terylene
- (d) Bakelite

(A.I.E.E.E. 2005)

B22. Which of the following is a fully fluorinated polymer?

- (a) Neoprene
- (b) Teflon
- (c) Thiokol
- (d) PVC

(A.I.E.E.E. 2005)

B23. Bakelite is obtained from phenol by reacting with

- (a) HCHO
- (b) $(CH_3CH_2)_2$
- (c) CH_3CHO
- (d) CH_3COCH_3

(A.I.E.E.E. 2008)

B24. The polymer containing strong inter molecular forces e.g. hydrogen bonding is

- (a) Polystyrene
- (b) Natural rubber
- (c) Teflon
- (d) Nylon 6, 6

(A.I.E.E.E. 2010)

B25. Thermosetting polymer bakelite is formed by the reaction of phenol with

- (a) CH_3CHO
- (b) HCHO
- (c) HCOOH
- (d) CH_3CH_2CHO

(A.I.E.E.E. 2011)

B26. The species which can serve as an initiator for the anionic polymerization is

- (a) HNO_3
- (b) $AlCl_3$
- (c) BuLi
- (d) $LiAlH_4$

(A.I.E.E.E. 2012)

B27. Which one is classified as a condensation polymer?

- (a) Acrylonitrile
- (b) Dacron
- (c) Neoprene
- (d) Teflon

JEE Main 2014

B28. Which polymer is used in the manufacture of paints and lacquers?

- (a) Polypropene
- (b) Polyvinyl chloride
- (c) Bakelite
- (d) Glyptal

JEE Main 2016

B29. Which of the following statement about low density polythene is false?

- (a) Its synthesis requires high pressure
- (b) It is a poor conductor of electricity
- (c) Its synthesis requires dioxygen as a powerful oxidant as a catalyst
- (d) It is used in the manufacture of buckets, dustbins etc.

JEE Main 2016

- B13. (d) B14. (d) B15. (a) B16. (c) B17. (d) B18. (d) B19. (a) B20. (e) B21. (b) B22. (b)
B23. a B24. (d) B25. (b) B26. (b) B27. b B28. (d) B29. (c)

Competition File

B30. The formation of which of the following polymers involves *anhydrous reaction*?

- (a) Nylon 6 (b) Bakelite
(c) Nylon 6,6 (d) Terylene (JEE Main 2017)

B31. Match list I with list II and select the correct answer using the codes given below

List I (Polymers)

List II (Monomers)

- | | |
|--------------------|--|
| 1. Buna-N | A. Phthalic acid and ethylene glycol |
| 2. Nylon-66 | B. Terephthalic acid and ethylene glycol |
| 3. Dacron | C. Hexamethylene diamine and adipic acid |
| 4. Glyptal plastic | D. Isobutylene and isoprene |
| | E. Acrylonitrile and butadiene |
- (a) 1-B, 2-A, 3-D, 4-E (b) 1-C, 2-D, 3-A, 4-B
(c) 1-D, 2-C, 3-B, 4-A (d) 1-E, 3-C, 2-A, 4-B
(e) 1-E, 2-C, 3-B, 4-A (Kerala C.E.T. 2007)

B32. Given the polymers

A = Nylon 6, 6; B = Buna-S; C = Polythene. Arrange these in decreasing order of their intermolecular forces

- (a) $A > B > C$ (b) $B > C > A$
(c) $B < C < A$ (d) $C < A < B$ (J.C.E. 2009)

B33. Natural polymer amongst the following is

- (a) Cellulose (b) Kodex
(c) Nylon (d) Terylene

(Orissa J.E.E. 2010)

B34. In bakelite, the rings are joined to each other through:

- (a) CH_2 (b) O



(A.M.U. Engg. 2010)

B35. Which one of the following is an example of co-polymer?

- (a) Buna-S (b) Teflon
(c) PVC (d) Polypropylene

(West Bengal J.E.E. 2010)

B36. Which one of the following is a co-polymer formed by condensation polymerisation?

- (a) Terylene (b) Buna-S
(c) Buna-N (d) Neoprene (K.C.E.T. 2011)

B37. The monomers used for preparation of nylon-2-nylon-6 are

- (a) caprolactam
(b) oxalene and amino caproic acid
(c) glycine and amino caproic acid

(d) hexamethylenediamine and adipic acid

(e) glycine and amino valeric acid (Kerala P.E.T. 2011)

B38. Monomers of bakelite are

- (a) phenol and formaldehyde
(b) phenol and acetaldehyde
(c) quinol and formaldehyde
(d) none of the above

(Odisha J.E.E. 2011)

B39. In Buna-S, the symbol 'Ba' stands for

- (a) 1-butene (b) *n*-butene
(c) 2-butene (d) butadiene

(Karnataka CET 2010)

B40. The repeating unit present in Nylon 6 is

- (a) $[\text{NH}(\text{CH}_2)_5\text{NHCO}(\text{CH}_2)_4\text{CO}]_n$
(b) $[\text{CO}(\text{CH}_2)_5\text{NH}]_n$
(c) $[\text{CO}(\text{CH}_2)_6\text{NH}]_n$
(d) $[\text{CO}(\text{CH}_2)_4\text{NH}]_n$
(e) $[\text{NH}(\text{CH}_2)_5\text{NHCO}(\text{CH}_2)_6\text{CO}]_n$ (Kerala P.E.T. 2013)

B41. Novolac, the linear polymer used in paints is

- (a) copolymer of buta-1, 3-diene and styrene
(b) obtained by the polymerization of methyl methacrylate
(c) initial product obtained in the condensation of phenol and formaldehyde in the presence of acid catalyst
(d) obtained by the polymerisation of caprolactam
(e) copolymer of melamine and formaldehyde

(Kerala P.E.T. 2014)

B42. Terylene is not a

- (a) copolymer (b) polyester fibre
(c) chain growth polymer (d) step growth polymer

(Karnataka CET 2014)

B43. Identify the heteropolymer from the list given below

- (a) Polythene (b) Nylon-6
(c) Teflon (d) Nylon-6,6

(MH-CET 2015)

B44. Which among the following polymers does NOT soften on heating?

- (a) Bakelite (b) Polythene
(c) Polystyrene (d) PVC (MH-CET 2015)

B45. Among cellulose, poly(vinyl chloride), nylon and natural rubber, the polymer in which intermolecular forces of attraction are weakest is

- (a) Nylon (b) Poly(vinyl chloride)
(c) Cellulose (d) Natural rubber

(IIT J.E.E. 2009)

B46. Correct statement for thermoplastic polymer is

- (a) It does not become soft on heating under pressure
(b) It can not be remoulded
(c) It is either linear or branched chain polymer
(d) It is cross-linked polymer

(MH-CET 2016)

- B30. (a) B31. (c) B32. (a) B33. (a) B34. (a) B35. (c) B36. (a) B37. (c) B38. (a) B39. (d)
B40. (b) B41. (c) B42. (c) B43. (d) B44. (a) B45. (d) B46. (c)

Competition File

- B47.** Bulletproof helmets are made from:
 (a) Lexan (b) Saran
 (c) Glyptal (d) Thiokol *MH CET 2016*
- B48.** Which of the following is not true?
 (a) In vulcanisation, the rubber becomes harder and stronger
 (b) Natural rubber has trans configuration at every double bond
 (c) Buna-S is a co-polymer of butene and styrene
 (d) Natural rubber is 1, 4-polymer of isoprene. *Karnataka CET 2016*
- B49.** On complete hydrogenation, natural rubber produces
 (a) ethylene-propylene copolymer
 (b) vulcanised rubber (c) polypropylene
 (d) polybutylene. *JEE Advance 2016*
- B50.** Which of the following is not a biodegradable polymer?
 (a) Glyptal
 (b) Poly(hydroxybutyrate-co- β -hydroxyvalerate)
 (c) PHBV
 (d) Nylon-2-Nylon-6 *(Karnataka C.E.T. 2017)*
- B51.** The monomers used in novolac, a polymer used in paints are
 (a) butadiene and styrene
 (b) butadiene and acrylonitrile
 (c) phenol and formaldehyde
 (d) melamine and formaldehyde *Karnataka C.E.T. 2017*
- B52.** Protein is a polymer made of
 (a) carbohydrates (b) amino acids
 (c) nucleic acids (d) carboxylic acids
 (e) polycyclic aromatics *(Kerala P.E.T. 2017)*
- B53.** Dacron is continuous filament yarn used in curtains, dress fabrics and pressure fire hoses. The reaction for preparing dacron is by the combination of which of the following?
 (a) Hexamethylene diamine and adipic acid
 (b) Caprolactam
 (c) Phenol and formaldehyde
 (d) Ethylene glycol and terephthalic acid *(J.K. CET 2018)*
- B54.** What is the IUPAC nomenclature of isoprene monomer present in natural rubber?
 (a) 2-Methyl-1, 3-butadiene
 (b) 1, 3-Hexadiene
 (c) 2, 3-Dimethyl-1, 3-butadiene
 (d) 2-Methyl-1, 3-pentadiene *(J.K. CET 2018)*
- B55.** Which one of the following is a condensation polymer?
 (a) PVC (b) Teflon
 (c) Dacron (d) Polystyrene *(W.H.J.E.E. 2018)*
- B56.** Which one of the following is a polyamide polymer?
 (a) Terylene (b) Nylon-6,6
 (c) Buna-S (d) Bakelite *Karnataka C.E.T. 2018*
- B57.** Among the following, the branched chain polymer is
 (a) polyvinyl chloride (b) bakelite
 (c) low density polythene (d) high density polythene *(Karnataka C.E.T. 2018)*
- B58.** Ziegler-Natta catalyst is used to prepare
 (a) low-density polythene (b) teflon
 (c) high-density polythene (d) nylon-6 *Karnataka C.E.T. 2018*

B47. a B48. b B49. a B50. a B51. c B52. b B53. d B54. a B55. c B56. b
 B57. (c) B58. (c)

C (MULTIPLE CHOICE QUESTIONS with more than one correct answers

- C1.** Which of the following are thermosetting polymers?
 (a) Melamine (b) Teflon
 (c) Polystyrene (d) Bakelite
- C2.** Which of the following polymers contain 1, 3-butadiene as one of the monomers?
 (a) ABS plastic (b) SBR
 (c) Saran (d) Natural rubber
- C3.** The addition homopolymers are
 (a) Styron (b) PMMA
 (c) Terylene (d) Bakelite
- C4.** Which of the following contain ethylene glycol as one of the monomers?
 (a) Melamine (b) Polystyrene
 (c) Glyptal (d) Terylene
- C5.** Which of the following are biodegradable polymers?
 (a) PHBV (b) ABS plastic
 (c) PCL (d) PVC
- C6.** Which of the following are condensation polymers?
 (a) Nylon-6 (b) Styron
 (c) PEA (d) Bakelite
- C7.** Which of the following can be used as plasticisers?
 (a) Cresyl phthalate (b) Diethyl phthalate
 (c) Polystyrene (d) Trimethyl phosphate
- C8.** Which of the following statements are correct?
 (a) Alkyl resins are addition polymers
 (b) Polystyrene is a thermoplastic
 (c) Dacron is a fibre
 (d) Natural rubber behaves as thermosetting polymer

Answers

C1. a, d C2. (a, b, d) C3. (a, b) C4. (c, d) C5. a, d C6. (a, d) C7. (a, b) C8. (b, c)

Competition File

Matrix Match Type Questions

Each question contains statements given in two columns, which have to be matched. Statements in Column I are labelled as A, B, C and D whereas statement/s in Column II are labelled as p, q, r and s. Match the entries of Column I with appropriate entries of Column II. Each entry in Column I may have one or more than one correct option from Column II. The answers to these questions have to be appropriately bubbled as illustrated in the following example.

If the correct matches are A-q, A-r, B-p, B-s, C-r, C-s and D-q, then the correctly bubbled matrix will look like the following.

	p	q	r	s
A	<input checked="" type="radio"/>	<input checked="" type="radio"/>	<input checked="" type="radio"/>	<input type="radio"/>
B	<input checked="" type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input checked="" type="radio"/>
C	<input type="radio"/>	<input type="radio"/>	<input checked="" type="radio"/>	<input checked="" type="radio"/>
D	<input type="radio"/>	<input checked="" type="radio"/>	<input type="radio"/>	<input type="radio"/>

(1) A p s B q r C p r D s (2) A p r B p C p s D q

Integer Type Questions

Integer Type: The answer to each of the following question is a single-digit-integer ranging from 0 to 9.

- The number of condensation polymers among the following
nylon 6, glyptal, orlon, terylene, bakelite, PVC, nylon 6, 6, melamine are
- How many of the following are synthetic rubbers?
Buna-S, polystyrene, Buna-N, neoprene, neoprene-thickol, PVC, terylene.

1. 6 2. 4 3. 5 4. 0 5. 8 6. 0

- Match the chemical substances in column I with type of polymers/type of bonds in column II.

Column I	Column II
A Cellulose	p natural polymer
B Nylon 6,6	q synthetic polymer
C Protein	r amide linkage
D Sucrose	s glycoside linkage

- Match the polymers in Column I with the characteristic noted in Column II.

Column I	Column II
A Buna-S	p Synthetic polymer
B Bakelite	q Biodegradable polymer
C Teflon	r Elastomer
D Isotactic acid	s Thermoplastic

- How many of the following are elastomers?
Buna-N, nylon 6, Buna-S, neoprene, natural rubber, vulcanized rubber, acrlon, orlon.
- The number of thermoplastic polymers among teflon, polythene, PVC, polystyrene, bakelite, nylon 6, melamine formaldehyde, PMMA are
- Number of synthetic polymers among PVC, nylon 6, starch, Buna-N, terylene, bakelite, neoprene, polyisoprene, nylon 6, 6, glyptal, cellulose are
- The total number of lone pairs of electrons in melamine is

JEE Advance 2019



NCERT

Exemplar Problems

Objective Questions

- Which of the following polymers of glucose is stored by animals?

- Cellulose
- Amylose
- Amylopectin
- Glycogen

Competition File

2. Which of the following is not a semisynthetic polymer?

- (a) cis-polyisoprene (b) Cellulose nitrate
(c) Cellulose acetate (d) Vulcanised rubber

3. The commercial name of polymethylacrylate is

- (a) Dacron (b) Orlon (acrilan)
(c) PVC (d) Bakelite

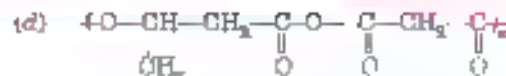
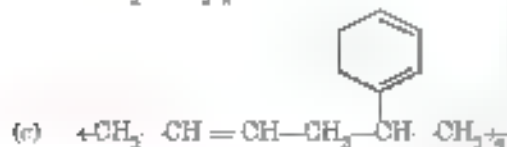
4. Which of the following polymer is biodegradable?

- (a) $+CH_2-C(=O)-CH_2-CH_2+$

(b)



5. In which of the following polymers ethylene glycol is one of the monomer units?



6. Which of the following statements is not true about low density polythene?

- (a) Tough
(b) Hard
(c) Good conductor of electricity
(d) Highly branched structure

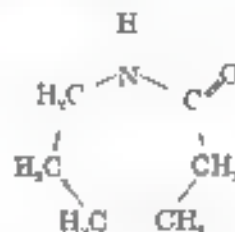


7. $+CH_2-C(CH_3)=CH-CH_2-$ is a polymer having



- (a) $+CH_2-CH=CH-CH_2+$ (b) $+CH_2-CH=CH-CH_2+$
(c) $+CH_2-CH=CH-CH_2+$ (d) $+CH_2-CH=CH-CH_2+$

8. Which of the following polymer can be formed by using the following monomer unit?



- (a) Nylon 6, 6 (b) Nylon 2-nylon 6
(c) Melamine polymer (d) Nylon-6

2. (a) 3. (b) 4. (c) 5. (a) 6. (c)

7. (a) 8. (d)

Multiple Choice Questions (Type-B)

Note In the following questions two or more options may be correct

9. Which of the following polymers need atleast one diene monomer for their preparation?

- (a) Dacron (b) Buna-S
(c) Neoprene (d) Novolac

10. Which of the following are characteristics of thermosetting polymers?

- (a) Heavily branched cross linked polymers.
(b) Linear slightly branched long chain molecules
(c) Become infusible on moulding so cannot be reused
(d) Soften on heating and harden on cooling, can be re-used.

11. Which of the following polymers are thermoplastic?

- (a) Teflon (b) Natural rubber
(c) Neoprene (d) Polystyrene

12. Which of the following polymers are used as fibres?

- (a) Polytetrafluoroethane (b) Polychloroprene
(c) Nylon (d) Terylene

13. Which of the following are addition polymers?

- (a) Nylon
(b) Melamine formaldehyde resin
(c) Orlon
(d) Polystyrene

14. Which of the following polymers are condensation polymers?

- (a) Bakelite
(b) Teflon
(c) Butyl rubber
(d) Melamine formaldehyde resin

Answers

9. (b), (c) 10. (a), (c) 11. (a), (d) 12. (c), (d) 13. (c), (d) 14. (a), (d)

Competition File

15. Which of the following monomers form biodegradable polymers?
 a) 3-hydroxybutanoic acid + 3-hydroxypentanoic acid
 b) Glycine + amino caproic acid
 c) Ethylene glycol + phthalic acid
 d) Caprolactam
16. Which of the following are example of synthetic rubber?
 a) Polychloroprene (b) Polyacrylonitrile
 c) Buna-N (d) cis-polyisoprene
17. Which of the following polymers can have strong intermolecular forces?
 a) Nylon (b) Polyethylene
 c) Rubber (d) Polyesters
18. Which of the following polymers have vinyl monomer units?
 a) Acrylic (b) Polyethylene
 c) Nylon (d) Teflon
19. Vulcanisation makes rubber
 (a) more elastic
 b. soluble in inorganic solvent
 (c) crystalline
 d) more stiff

Answers

15. a, b 16. a, c 17. a, d 18. a, b, d 19. a, d

Note Match the items of Column I and Column II in the following questions

20. Match the polymer of column I with correct monomer of column II

Column I	Column II
(a) High density polythene	(i) Isoprene
(b) Neoprene	(ii) Tetrafluoroethene
(c) Natural rubber	(iii) Chloroprene
(d) Teflon	(iv) Acrylonitrile
(e) Acrylic	(v) Ethene

21. Match the polymers given in Column I with their chemical names given in Column II

Column I	Column II
a. Nylon 6	(i) Polyvinyl chloride
b. PVC	(ii) Polyacrylonitrile
c. Arilan	(iii) Polymethylacetal
d. Natural rubber	(iv) Low density polythene
e. LDP	(v) cis-polyisoprene

22. Match the polymers given in Column I with their commercial names given in Column II

Column I	Column II
(a) Polyester of glycol and phthalic acid	(i) Novolac
(b) Copolymer of 1,3-butadiene and styrene	(ii) Glyptal
(c) Phenol and formaldehyde resin	(iii) Buna-S
(d) Polyester of glycol and terephthalic acid	(iv) Buna-N
(e) Copolymer of 1,3-butadiene and acrylonitrile	(v) Dacron

23. Match the polymers given in Column I with their main applications given in Column II

Column I	Column II
a. Bakelite	(i) Unbreakable crockery
b. Low density polythene	(ii) Non-stick cookware
c. Melamine-forma	(iii) Packaging material for shock absorbance
d. Nylon 6	(iv) Electrical switches
e. Polytetrafluoroethane	(v) Squeeze bottles
f. Polystyrene	(vi) Tyre cords

24. Match the polymers given in Column I with the preferred mode of polymerisation followed by their monomers

Column I	Column II
a. Nylon 6 6	(i) Free radical polymerisation
b. PVC	(ii) Ziegler-Natta polymerisation or coordination polymerisation
c. HRP	(iii) Anionic polymerisation
	(iv) Condensation polymerisation

25. Match the polymers given in Column I with the type of linkage present in them given in Column II

Column I	Column II
(a) Terylene	(i) Glycosidic linkage
b. Nylon	(ii) Ester linkage
(c) Cellulose	(iii) Phosphodiester linkage
d. Protein	(iv) Amide linkage
e. RNA	

20. (a) → (ii), (b) → (iii), (c) → (i), (d) → (iv), (e) → (v)

22. (a) → (iv), (b) → (ii), (c) → (i), (d) → (v), (e) → (iii)

24. (a) → (iv), (b) → (ii), (c) → (i)

21. a → (ii), b → (i), c → (iii), d → (iv), e → (v)

23. (a) → (iv), (b) → (v), (c) → (iii), (d) → (ii), (e) → (i), (f) → (vi)

25. (a) → (ii), (b) → (iv), (c) → (i), (d) → (iii), (e) → (i)

Competition File

26. Match materials given in Column I with the polymers given in Column II

Column I	Column II
a. Natural rubber latex	(i) Nylon
b. Wood laminates	(ii) Neoprene
(c) Ropes and fibres	(iii) Dacron
(d) Polyester fabric	(iv) Melamine formaldehyde resins
e. Synthetic rubber	(v) Urea-formaldehyde resins
f. Unbreakable crockery	(vi) cis-polyisoprene

27. Match the polymers given in Column I with their repeating units given in Column II

Column I	Column II
a. Acrylic	(i) $-CH_2-CH-$
	Cl H

b. Polystyrene	(ii) $-CH_2-CH=CH-CH_2-$
c. Neoprene	(iii) $-CH=CH-CH=CH-$
(d) Novolan	(iv) $-CH=CH-$
	Cl OH
(e) Buna-N	(v) $-CH_2-CH-$
	Cl OH

26. a' → (vi), (b) → (v), (c) → (iii), (d) → (iv), (e) → (ii), (f) → (i) 27. (a) → (iv), (b) → (ii), (c) → (iii), (d) → (v), (e) → (i)

Assertion and Reason Type Questions

Note : In the following questions a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices

- (a) Assertion and reason both are correct statement but reason does not explain assertion.
 (b) Assertion and reason both are correct statements and reason explains the assertion.
 (c) Both assertion and reason are wrong statement.
 (d) Assertion is correct statement and reason is wrong statement.
 (e) Assertion is wrong statement and reason is correct statement.
28. **Assertion :** Rayon is a semi synthetic polymer and is taken as a better choice than cotton fabric.
Reason : Mechanical and aesthetic properties of cellulose can be improved by acetylation.
29. **Assertion :** Most of the Synthetic polymers are not biodegradable.

Reason : Polymerisation process induces coise character in organic molecules.

30. **Assertion :** Olefinic monomers undergo addition polymerisation.
Reason : Polymerisation of vinyl chloride is initiated by peroxide/persulphates.
31. **Assertion :** Polyamides are best used as fibres because of high tensile strength.
Reason : Strong intermolecular forces (like hydrogen bonding within polyamides) lead to close packing of chains and increase the crystalline character, hence, provide high tensile strength to polymers.
32. **Assertion :** For making rubber synthetically isoprene molecules are polymerised.
Reason : Neoprene is a polymer of chloroprene is a synthetic rubber.
33. **Assertion :** Network polymers are thermosetting.
Reason : Network polymers have high molecular mass.
34. **Assertion :** Polytetrafluoroethene is used in making non-stick cookwares.
Reason : Fluorine has highest electronegativity.

Competition File

Hints & Explanations for Difficult Objective Type Questions

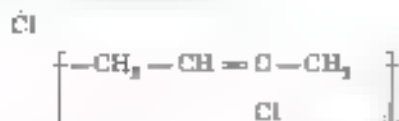
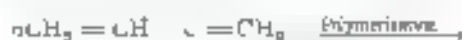
A. mcq with only one correct answer

- A16 a Caprolactam is a monomer of nylon-6
A24 c Benzoquinone inhibits the free radical polymerisation of vinylic derivatives.
A28 c Terylene is



B. mcq from Competitive Examinations

- B2 d) Nylon 6,6 is prepared by condensation polymerisation.
B4 a Neoprene is a polymer of chloroprene



- B5 b Nylon-6, 0 is an example of Glue
B6 a Nylon is an example of polyamide
B7 a $\text{CH}_2=\underset{\text{Cl}}{\text{C}}-\text{CH}=\text{CH}_2$ Chloroprene is monomer of neoprene

- B12 c Natural rubber has all cis-configuration of double bonds.

- B14 d) Cross linked or network polymers are usually formed from bi-functional or tri-functional monomers b and contain strong covalent bonds between various linear polymer chains (a, like melamine, bakelite, etc. c)

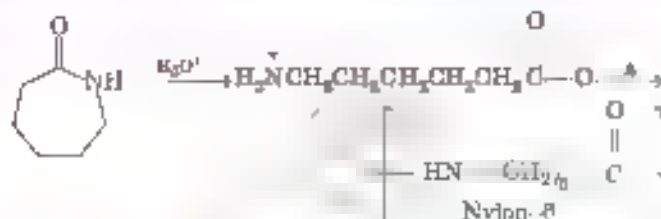
- B16 d) The monomer of natural rubber is isoprene and not butadiene

- B24 d) Nylon 6,6 has strong intermolecular forces. It has amide linkages and therefore, has strong hydrogen bonding between two polyamide chains.

- B27 b Dacron is a condensation polymer formed by the condensation of -OH group of ethylene glycol and -COOH group of terephthalic acid with the elimination of water molecules

- B29 d) Buckets and dustbins are manufactured from high density polythene

- B30 a Formation of nylon-6 involves hydrolysis of its monomer (caprolactam) in initial stage



- B32 (a) In nylon 6, 6; amide linkage is present. Amide linkage is polar, hence is strongest. Out of Buna-S and polythene, Buna-S has greater surface area. Hence it has stronger intermolecular forces.

- B38 (a) Terylene is a copolymer formed by the condensation of terephthalic acid and ethylene glycol.

- B41 (c) Novolac is initial product obtained in the condensation of phenol and formaldehyde.

- B42 (c) Terylene is a condensation polymer and is not a chain growth polymer

- B47 (a) Bullet proof helmets are made from lexan

- B48 b) Natural rubber has cis-configuration at every double bond.

- B52 b) Proteins are condensation polymers of α -amino acids

- B33 (d) Dacron is prepared by condensing terephthalic acid and ethylene glycol

- B54 (a) $\text{CH}_2=\underset{\text{CH}_3}{\text{C}}-\text{CH}=\text{CH}_2$ 2-Methyl but 1, 3-diene

- B55 (c) Dacron is a condensation polymer

- B58 (b) Nylon-6,6 is a polyamide

- B57 (c) PVC and high density polythene are linear polymers low density polythene is branched chain polymer while bakelite is cross linked polymer

NCERT Exemplar Problems : MCQs Type-I

- d) Glycogen is stored by animals
- a) Cis-polyisoprene is a natural rubber
- (c) It is not a good conductor of electricity
- a) The repeating structural unit is $\text{CH}_2\text{C}(\text{CH}_3)_2$ and hence the monomer is isobutylene $\text{CH}_2=\text{C}(\text{CH}_3)_2$
- d) The monomer is caprolactam and hence the polymer is nylon-6

NCERT Exemplar Problems : MCQs Type-II

- b, c) Buna-S 1,3-butadiene, neoprene (2-chlorobut-1,3-diene)
- (a, d) Teflon and polystyrene are thermoplastics
- c, d) Nylon and terylene are used as fibres.
- a, d) Vulcanisation of rubber makes it more elastic and stiff

CHEMISTRY IN EVERYDAY LIFE



1985-1986

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Chemistry plays a very important role in our everyday life. The principles of chemistry have been used for the service of mankind since its very beginning. Our daily needs of food, clothing, shelter, potable water, medicines, etc. are in one or the other manner connected with chemical compounds, processes and principles. **We always owe a debt to chemists** for their important contributions for giving us *life saving drugs, synthetic fibres, synthetic detergents, variety of cosmetics, preservatives for our food, fertilizers, pesticides, paper, glass, strong materials, plastics, beautiful paints, etc.* There is no aspect of our life that is not affected by the developments in chemistry. In fact chemistry is the single branch of science which profoundly influences the existence of human beings and the habitat. Thus, the mankind owes much to chemistry because it has improved the quality of life.

SOME BASIC TERMS USED IN MEDICINAL CHEMISTRY

Medicinal chemistry deals with the study of drugs. It involves their isolation and synthesis, characterisation and establishing links between their chemical structure and biological activity to be used in medicine for the treatment and cure of diseases.

Drugs

Drug is defined as **a substance / chemical compound, used for the purpose of diagnosis, prevention, relief or cure of a disease.**

The word drug is derived from the French word "*drogue*" meaning herb. Drugs are chemicals of low molecular mass about 100 to 500 u. These interact with macromolecular targets in the body and produce a biological response.

When the drug has useful action as in the diagnosis, prevention, treatment and cure of a disease, called **therapeutic effect**, it is called **medicine**. The use of chemicals for therapeutic effect is called **chemotherapy**. On the other hand, if the drug causes a harmful effect on the body such as side effects or toxicity, the drugs behave as **poisons**. These side effects or toxicity may also occur if the doses taken are higher than recommended. Drugs may be administered by oral, intravenous injections, intramuscular route, subcutaneous route, injection beneath the skin, inhalation or by local application. The route of administration of a drug is determined by its physical and chemical properties, the site of desired action and the time course of the response desired.

Classification of Drugs

Drugs can be classified into the following simple ways

(i) On the basis of pharmacological effect

This type of classification is based on the pharmacological effect of the drugs. For example, *analgesics* have pain relieving effect, *antipyretics* help in lowering the body temperature, *antiseptics* kill or arrest the growth of microorganisms, *antidepressants* help in changing mood, etc. This classification is very useful for doctors because it provides them the whole range of drugs available for the treatment of a particular type of disease.

(ii) On the basis of action on a particular biochemical process

This type of classification is based on the action of a drug on a particular biochemical process. For example, all antihistamine drugs inhibit the action of histamine compound which causes inflammation in body and allergic reactions. The drugs which are used to block the action of histamines are known as antihistamines. Similarly, drugs related to gastro intestinal mobility and secretion process (gastro intestinal tract) are grouped together.

(iii) On the basis of chemical structure

The drug may also be classified on the basis of their chemical structure. The drugs having similar chemical structures may have similar pharmacological activity. For example, alcohols are known to possess hypnotic, analgesic and anesthetic action. Sulphonamides have common structural formula as shown.

Most of these show antibacterial properties.

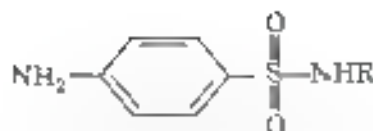
(iv) On the basis of molecular targets

This classification is based on the molecular targets and is considered as the most useful mode of classification for medicinal chemists. Drugs usually interact with the biomolecules such as carbohydrates, proteins, lipids and nucleic acids known as **target molecules** or **drug targets**. Drugs possessing same common structural features may have the same mechanism of action on specific drug target molecules. Many enzymes and receptors in the cells have some common drug targets.

Interaction of Drugs with Targets

Drugs interact with macromolecules such as carbohydrates, proteins, lipids and nucleic acids. These macromolecules are known to perform different functions in the body. For example, different proteins perform several roles in the body.

- The proteins which perform the role of biological catalysts are called **enzymes**.
- The proteins which are very vital for communication system in the body are called **receptors**.
- The proteins which carry the polar molecules across the cell membrane are called **carrier proteins**.



Structure of sulphonamides

Similarly **nucleic acids** are responsible for genetic information in the cells while carbohydrates and fats are the structural part of the cell membranes.

(1) Enzymes as drug targets

(a) Catalytic action of Enzymes

We have already learnt in Unit 5, the role of enzymes in catalysing a reaction. In their catalytic activity, the enzymes act similar to **lock and key principle**. The enzymes perform the two main functions

1. **The first function of an enzyme is to hold the substrate for a chemical reaction.** The substrate is held in active site of enzymes in such a position so that it can be readily and effectively attacked by the reagent. The substrates are bound to the amino acid groups of the proteins, called amino acid residues, on the active sites of the enzyme through different chemical forces such as ionic bonding, hydrogen bonding, van der Waals' forces, ion-dipole interactions and dipole-dipole interactions (Fig. 1). The nature of the binding gives an indication of the duration of action. For example, whenever, a drug is bound by covalent bonding a prolonged duration is expected. However, these binding interactions should be strong enough to hold the substrate long enough so that the enzyme can catalyse the reaction, but weak enough so as to allow the products to depart.

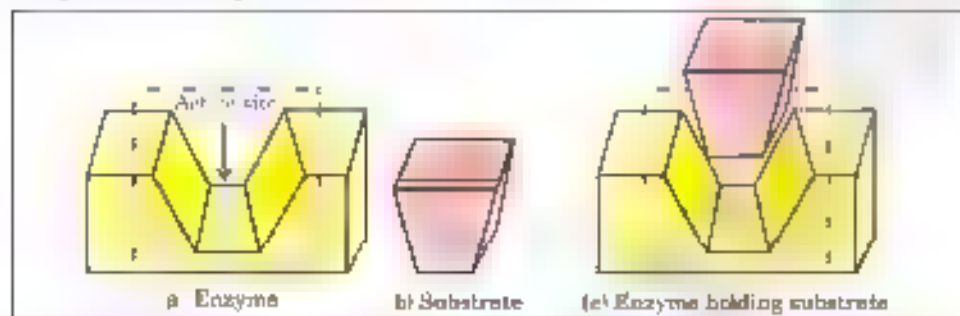


Fig.1. (a) Active site of an enzyme (b) substrate and (c) substrate held in active site of the enzyme.

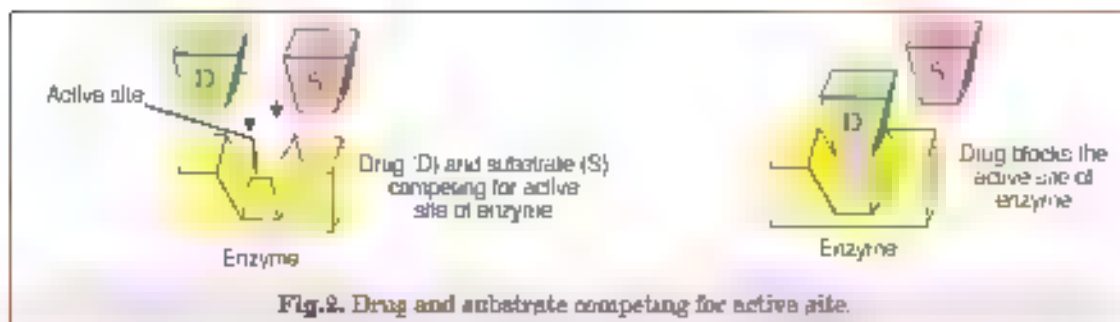
2. **The second function of enzyme is to provide functional groups which will attack the substrate and carry out the chemical reaction.** This function is performed by some other amino acid residues of protein, present on the active sites of the enzyme. These provide free functional groups such as $-OH$, $-COOH$, $-SH$ etc. to attack the substrate. For example, if amino acid residue is present nearby the substrate held in active site, then its $-OH$ group is free to act as nucleophile in the enzyme catalysed reaction.

(b) Drug-Enzyme Interaction

The main role of drugs is to either increase or decrease the rate of enzyme catalysed reactions. Inhibition of enzymes is a common role of drug action. Many drugs show their effects by modifying the function of enzymes. The enzyme inhibitors can block the binding site and prevent the binding of the substrate or can inhibit the catalytic activity of the enzyme. Some of the enzyme inhibitors are useful therapeutic agents. For example, inhibitors of enzyme monoamine oxidase (MAO inhibitor) are used as antidepressant agents. The drugs can inhibit the attachment of substrate in active site of the enzymes in following two ways

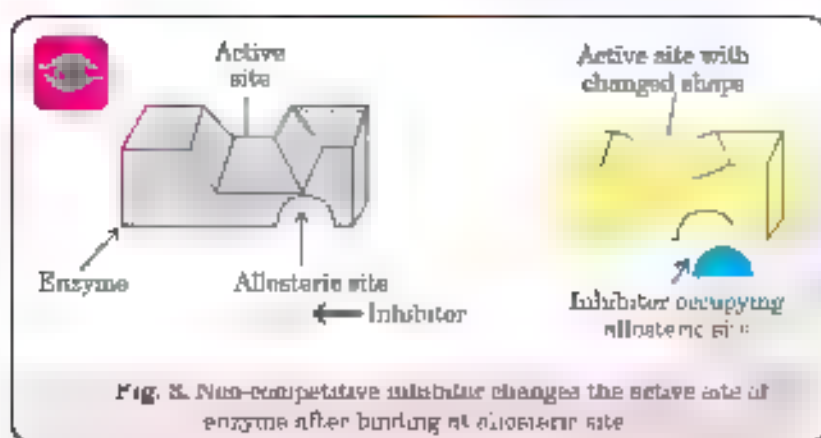
(i) Competitive inhibition

The substrate and inhibitor cannot bind to the enzyme at the same time. This usually results from the inhibitor having an affinity for the active site of the enzyme where the substrate also binds. Therefore, the substrate and the inhibitor compete for the approach to the enzyme's active site. Such drugs are called competitive inhibitors (Fig. 2) shown ahead.



(ii) Non-competitive inhibition

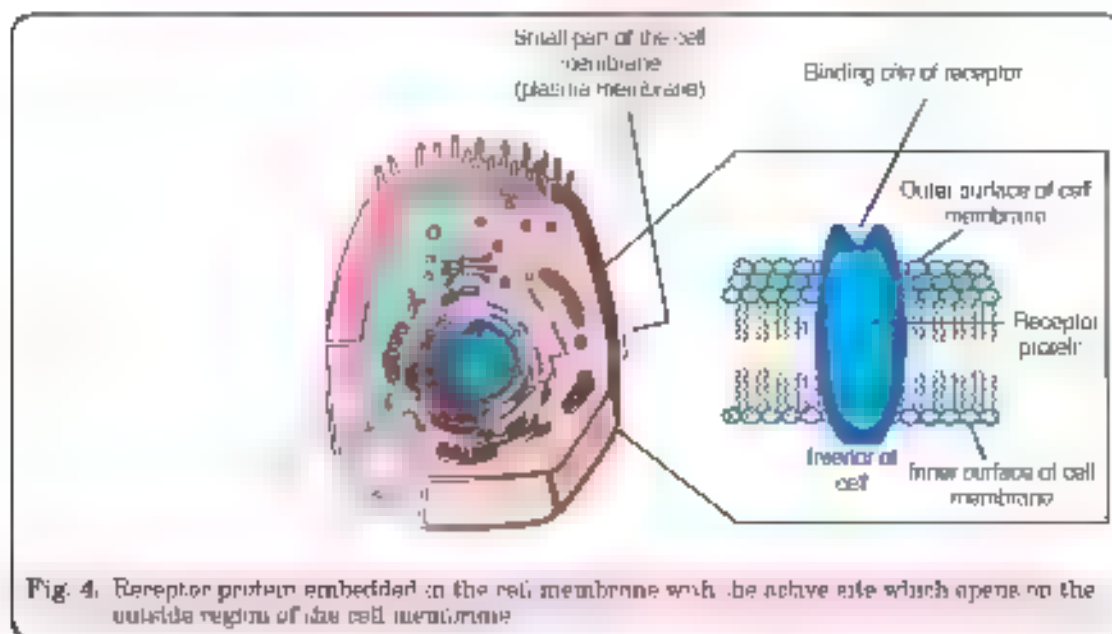
In this type, drugs don't bind to the active site but bind to a different site of enzyme called **allosteric site** (Fig. 3). The binding of inhibitor at a allosteric site changes the shape and conformation of active site so that the affinity of the substrate for the active site is reduced.



It may be noted that if the bond formed between enzyme and inhibitor is strong covalent bond and therefore cannot be broken easily then the enzyme gets blocked permanently. The body then degrades the enzyme-inhibitor complex and synthesises new enzyme.

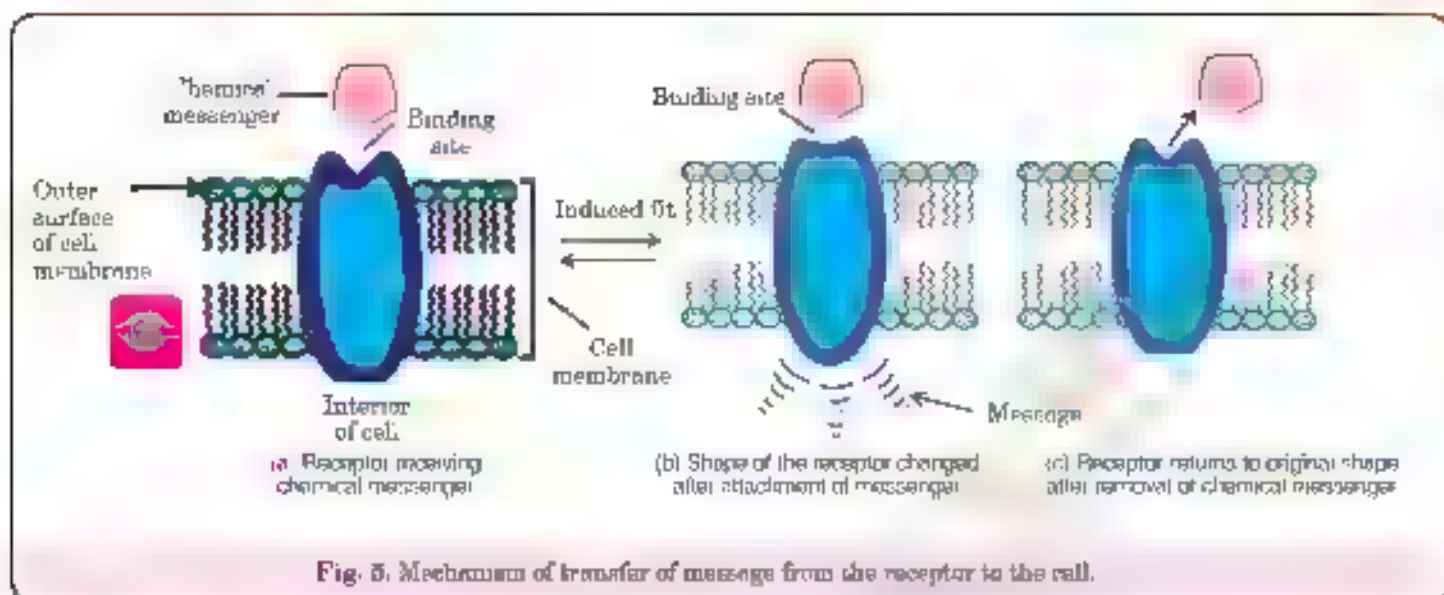
2. Receptors as Drug Targets

Receptors or proteins majority of which are embedded in cell membranes. These are embedded in the cell membranes in such a way that their small part possessing active site projects from one surface of the membrane and opens up on the outside region of the cell membrane. This is shown in Fig. 4.



As we know in the central nervous system, the information is conveyed and received by neurons. The information is transmitted from one neuron to another by nerve pulse. The message between two neurons and that between neurons to the muscles is communicated with the help of chemicals known as **chemical messengers**. These are received at the binding site of the receptor proteins (Fig. 5 a). To accommodate

the messenger, the shape of the receptor changes. After the transfer (Fig. 5 b) of the message, the chemical messenger departs and the active site of the receptor protein returns to its original shape (Fig. 5 c). The complete process of transfer of message from the receptors to the cell is shown in Fig. 5, and results in the transfer of the message to the cell. Thus, chemical messengers give messages to the cell without entering into the cell.



There are two types of chemical messengers which are involved in the message transfer. These are

- Hormones
- Neurotransmitters

➤ Hormones

These are the chemical substances which are produced in ductless glands known as endocrine glands. They enter the blood stream and are carried to different parts of the body by the blood stream where they activate all the receptors which recognise them for message transfer. They are not deactivated very quickly. For example, adrenaline (epinephrine) is a hormone which is released from adrenal medulla in situations of stress or danger. It prepares the body (humans or animals) for physical exercise to bear the stress.

➤ Neurotransmitters

These are small molecules which help in the transfer of nerve messages. Some common examples of neurotransmitters are acetylcholine, serotonin, dopamine, etc. A neurotransmitter is released by nerve endings and gets bound to the active site (binding site) of the closely placed target receptor for a very short time to transfer message to it. It then departs quickly unchanged after transferring the message. The receptor then forwards the message inside the cell. After leaving the active site, the neurotransmitters undergo degradation and lose their capabilities of transferring messages, i.e., they are deactivated. The degraded products go back to the nerve endings to become active messages again. In this way, the cycle of message transfer is repeated again.

The mechanism of activating a receptor is same regardless of whether the messenger is a hormone or a neurotransmitter.

Based on the activity of drugs, these may be classified into two main types

(i) Agonists

A drug which stimulates or activates the receptor to initiate a physiological response is called **agonist**. For example, acetylcholine is an agonist for the cholinergic receptor. These mimic the natural messenger by switching on the receptor. These are useful when there is lack of natural chemical messenger.

(ii) Antagonists

The drugs which occupy the receptor sites without producing any response are called **antagonists**. These bind to the receptor site and inhibit its natural function. These stop the agonists from stimulating the receptors.

There are a large number of receptors in the body which interact with different chemical messengers. These receptors have binding sites with different shapes, structure and amino acid composition and therefore



➤ Do drugs have side effects?

➤ One of the major problems of pharmacology is that no drug produces only a single effect. In addition to normal desired **therapeutic effect**, drugs may cause other effects which may either be beneficial or harmful. The side effects arise because a drug may bind to more than one type of receptor. For example, an anti-depressant drug is to interact with serotonin receptor. However, side effect may occur if the drug interacts with histamine or acetylcholine receptors. The side effect may also arise if the degraded product of the drug is biologically active and interacts with some other receptors.

show selectivity for one chemical messenger over the other. The receptor which interact with a specific chemical messenger may differ in its binding sites. For example, there are two types of adrenergic receptors named as α -adrenergic and β -adrenergic, both of which can bind epinephrine. However, these two types have slightly different binding sites and therefore, it is possible to design drugs which will bind better with α - or β -adrenergic receptor. These are not distributed evenly throughout the body. For example, the heart has more of β - than α -adrenergic receptors while tissues have more of α - than β -adrenergic receptors. Therefore, the drug designed to interact with β - form will act on heart rather than on tissues.

CHEMICALS IN MEDICINES AND HEALTH CARE

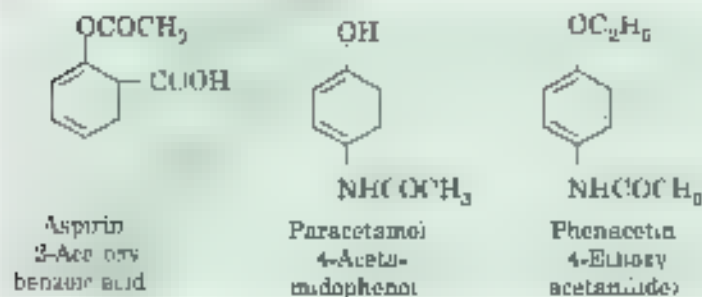
The chemical substances used for treatment of diseases and for reducing suffering from pain are called medicines or drugs.

The term **chemotherapy** is used for the science in which suitable chemicals are used for the treatment of diseases. These chemicals have specific effects for destroying the invading organisms without harming the cells of the body. Like the ancient practices of treatment of disease like Ayurvedic, the Unani systems or the modern allopathic system, the drugs used are chemical compounds of natural or synthetic origin. Let us discuss some specific classes of drugs used in allopathic system. Some of the medicinal compounds are discussed below.

1. Antipyretics

The chemical substances which are used to lower the temperature of the body in high fever are called antipyretics.

Examples: Aspirin (acetyl salicylic acid), paracetamol and phenacetin.



Aspirin is prepared by acetylation of salicylic acid using a mixture of acetic anhydride and glacial acetic acid.



2. Analgesics

The chemical substances which are used to relieve pains without causing impairment of consciousness, mental confusion, incoordination or paralysis or some other disturbances of nervous system are called analgesics.

These are of two types

(i) Non-narcotic (non-addictive) drugs

(ii) Narcotic drugs

1. Non-narcotic drugs: The common non-addictive analgesics are aspirin and paracetamol.

Aspirin (2-acetoxybenzoic acid) is most familiar example. It inhibits the synthesis of compounds known as prostaglandins which stimulate inflammation.

Health-Check

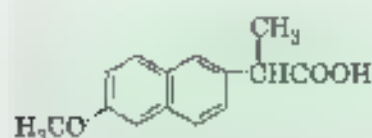


❑ Aspirin is an important non-narcotic drug. But overdoses of aspirin should be avoided.

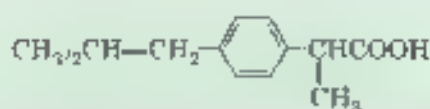
► Despite the popularity of aspirin, it is supposed to be toxic to the liver. It gets hydrolysed in stomach giving salicylic acid which sometimes causes bleeding in stomach. Therefore, overdosage and its use in empty stomach should be avoided. Calcium and sodium salts of aspirin are more soluble and less harmful.

in the tissues and cause pain. These drugs are effective in relieving skeletal pain such as that due to arthritis. Aspirin has also been very popular because it has antipyretic (temperature lowering) properties. Now aspirin also finds use in the prevention of heart attack because it has anti blood clotting action. In addition many other potential applications of aspirin presently under investigation, include pregnancy related complications, viral inflammation in AIDS patients, Alzheimer's disease, dementia, cancer, etc.

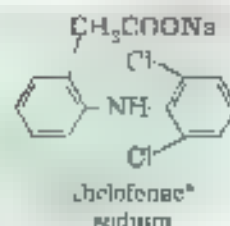
Because of shortcomings of aspirin, other analgesics like **naproxen**, **ibuprofen** and **diclofenac sodium or potassium** find use as alternatives.



Naproxen*

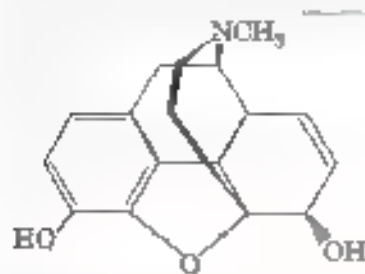


Ibuprofen*

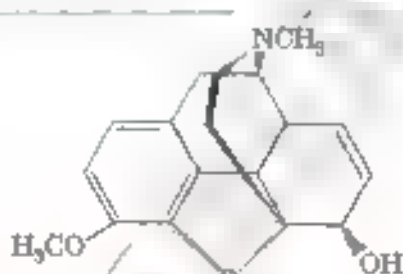


Diclofenac* sodium

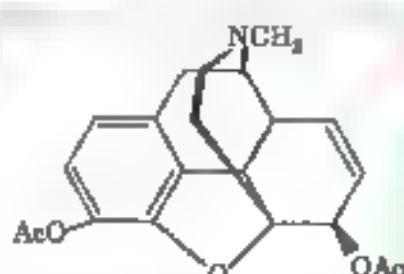
2 Narcotic drugs. Certain narcotics (which produce sleep and unconsciousness) are also used as analgesics. For example, morphine and its derivatives codeine, heroin, marijuana are used in severe pain as analgesics. These are known to be habit forming. When used in medicinal doses, these relieve pain and produce sleep. However, in excessive (poisonous) doses these produce stupor, coma, convulsions and ultimately leading to death. These narcotics are also referred to as **opiates** because they are obtained from the opium poppy.



Morphine



Codeine



Heroin

These analgesics are mainly used for the relief in postoperative pains, cardiac pain, and pains related to child birth and terminal cancer.

It may be noted that even now aspirin is the drug of choice for the prevention of heart attacks and as a reliever of pain in angina.

3. Tranquilizers

The chemical substances used for the treatment of stress, fatigue, mild and severe mental diseases are called tranquilizers.

Tranquilizers are neurologically active drugs which affect the message transfer mechanism from nerve to receptor. These are used to relieve or reduce mental tension, irritability, excitement and anxiety leading to calmness. These form an essential component of sleeping pills. They act on higher centres of nervous system. These are also called psychotherapeutic drugs. These drugs make the patient passive and help to control their emotional distress or depression. These also help to restore confidence and the patient's work with full capacities which they already have.

It may be noted that the narcotic drugs are known to be habit forming i.e. addictive drugs. Therefore, to guard against addiction and misuses these are not sold without prescription.

Tranquilizers and analgesics are neurological active drugs. These affect the message transfer mechanism from the nerve to receptor.

* All complicated structures are non-evaluative

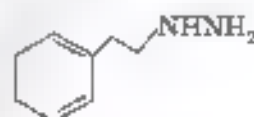
The word tranquilizer is derived from the word *tranquillus* meaning calm.

Tranquilizers are essential components of sleeping pills.

Examples. There are various types of tranquilizers which function by different mechanisms. The most common one is **noradrenaline** which induces a feeling of well being and helps in changing mood. It is one of the neurotransmitter that plays an important role in mood changes. If the level of noradrenaline is low due to certain reasons, then the signal sending activity of the hormone becomes low and the person suffers from depression. In such cases the patient needs **antidepressant drugs** which inhibit the enzymes which catalyse the degradation of noradrenaline. If the enzyme is inhibited, the metabolism of important neurotransmitter is slowed down and this can activate its receptor for longer periods of time and therefore counteract the effect of depression. The commonly used antidepressant drugs are **iproniazid** and **phenelzine**.



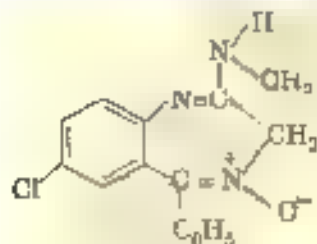
Iproniazid



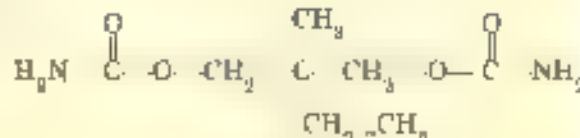
Phenelzine (Nardil)

Some other most commonly used tranquilizers are barbituric acid and its derivatives such as *veronal*, *amytal*, *mebutal*, *seconal* and *luminal*.

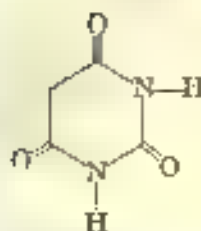
These derivatives are called **barbiturates**. These are hypnotic or sleep producing agents. In addition to barbiturates, a large number of other non-hypnotic tranquilizers are known. For example, *chlorodiazepoxide* and *meprobamate* are relatively mild tranquilizers suitable for relieving tension.



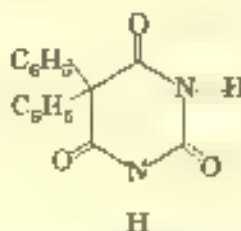
Chlorodiazepoxide



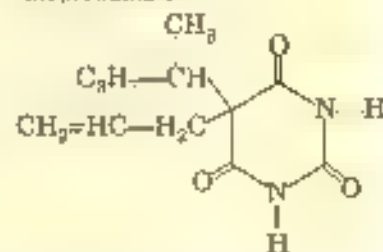
Meprobamate



Barbituric acid

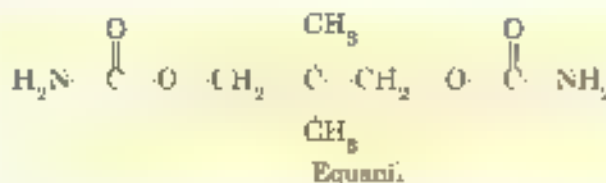


Luminal



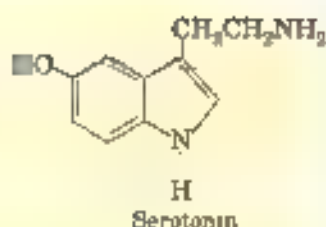
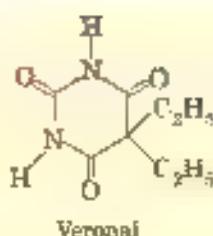
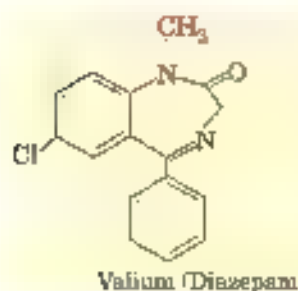
Seconal

Equanil is also an important tranquilizer used in depression and hypertension.



Equanil

Some other substances used as tranquilizers are *valium*, *diazepam*, *veronal*, *serotonin*, etc.



4. Antiseptics and Disinfectants

Antiseptics

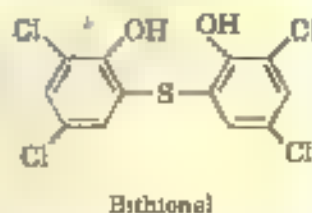
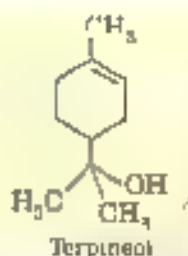
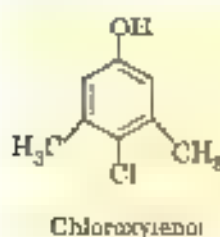
The chemical substances which are used to either kill or prevent the growth of micro-organisms are called antiseptics.

These are not harmful to living tissues and can be safely applied on wounds, cuts, ulcers, diseased skin surfaces. These are also used to reduce odours resulting from bacterial decomposition of the body or in the mouth. They are, therefore, mixed with deodorants, face powders and breath purifiers. We all must be familiar with antiseptic creams like *furacin*, *soframycin*, etc.

The common examples of antiseptics are:

(i) **Dettol** is an antiseptic. It is a mixture of chloroxylenol and terpineol in a suitable solvent. Chloroxylenol has both antiseptic and disinfectant properties.

(ii) **Bithional** is antiseptic which is generally added to medicated soaps to reduce the odour produced by bacterial decomposition of organic matter on the skin.



(iii) **Iodine** is powerful antiseptic. It is used as a **tincture of iodine** which is 2–3% iodine solution of alcohol-water.

(iv) A dilute aqueous solution of **boric acid** is used as a weak antiseptic for eyes. It also forms a part of antiseptic baby talcum powders.

(v) **Iodoform** is also used as an antiseptic powder for wounds.

(vi) **Hydrogen peroxide** is also used as a mild antiseptic under the name **perhydrol** for washing wounds, teeth, ears, etc.

(vii) **Salol** (phenyl salicylate) is used as an intestinal antiseptic for chronic ailments.

(viii) **Potassium permanganate** (KMnO_4) is used as antiseptic in dilute solutions.

(ix) **Amyl metacresol** (5-methyl-2-pentyl phenol) is an antiseptic which is used commonly as mouthwash or gargles in infections of the mouth and throat.

(x) Some organic dyes are also effective antiseptics. These are used for the treatment of infectious diseases. The common examples of antiseptic dyes are **gentian violet** and **methylene blue**.

Disinfectants

The chemical substances which are used to kill micro-organisms but they cannot be applied on living tissues are called disinfectants.

NOTE

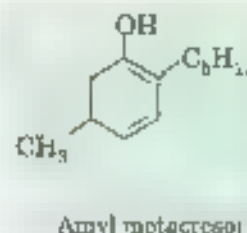
It may be noted that different terms are used for drugs which are used to cure mental diseases. Some of these terms are

(i) **Sedatives**. These act as depressant and suppress the activities of central nervous system. They are given to patients who are mentally agitated and violent. Sedatives give a feeling of calmness, relaxation or drowsiness in the body. Their high doses induce sleep. The common sedatives are *valium*, *barbiturates* (obtained from barbituric acid).

(ii) **Antidepressants**. These drugs are given to patients with shattered confidence. These produce a feeling of well being and confidence in the person of depressed mood. Therefore, these are also called *mood booster drugs*. The common examples are *amphetamines*, *cocaine*, *mephedrine*, etc.

(iii) **Hypnotics**. These are also known as **tranquillizers** and are used to reduce mental tension and anxiety. The lower doses of hypnotics or tranquillizers generally do not induce sleep.

(iv) **Narcotics**. These act as depressant and analgesic. They reduce tension and anxiety and also reduce pain. The common examples are *opium*, *heroin*, *pethidine*.



Therefore disinfectants are **not** micro-organisms and these are not safe for living tissues. Disinfectants play a major role in water and septage public health sanitation. These are commonly applied to inanimate objects such as floors, drainage system, instruments, etc.

The same substance can act as a disinfectant as well as antiseptic depending upon its concentration. For example a 0.2% solution of **phenol** acts as antiseptic and its 1% solution acts as disinfectant.

Some other common examples of disinfectants are

(i) Cl_2 is used for making water fit for drinking at a concentration 0.2 to 0.4 ppm.

(ii) Low concentrations of **sulphur dioxide** are used for sterilising and preservation of squashes.

(iii) A naturally occurring phenol derivative **thymol** is used as a powerful disinfectant than phenol.

(iv) A solution of **oresols** (i.e., *o*-, *m*-, or *p*-methylphenols) in soapy water is called **lysol** and is used as a disinfectant for floors.

5. Antimalarials

The chemical substances used for the treatment of malaria are called **antimalarials**.

The alkaloid **quinine** has been used as an antimalarial for a long time. These days a number of synthetic drugs have been prepared for the treatment of malaria. For example **chloroquine**, **primaquine**, **pyrimaquine**, etc.

6. Antimicrobials

These are the chemical substances used to cure infections due to micro-organisms.

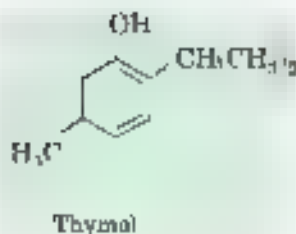
The diseases of human beings and animals may be caused by a variety of micro-organisms such as bacteria, viruses, fungi etc. The micro-organisms are extremely small organisms which can be seen only with a microscope. These are also called **microbes**. Any organism which causes disease is called **pathogen**. However, body possesses an efficient natural defence mechanism which guards itself from against potential pathogenic microbes. The skin is a barrier to microbes. Our body secretes substances which kill the microbes or inhibit their growth. The common examples of secretions are lysozyme in fluid in the eyes, mucus in tears, saliva, secretin, saliva, fatty acids and lactic acid in sweat and sebaceous secretions and **hydrochloric acid** in stomach. The pathogens reach the tissues due to a breach in defence mechanism and cause infection. Invasion and multiplication of an organism in a host that destroys the normal cell metabolism and cause physiological disturbances to the body which appears in the form of some disorders or diseases. In addition, toxic substances (toxins) produced by the microbes may adversely affect the tissues or organs of the host.

The control of microbial diseases can be achieved by the following three ways

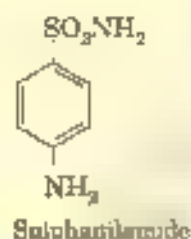
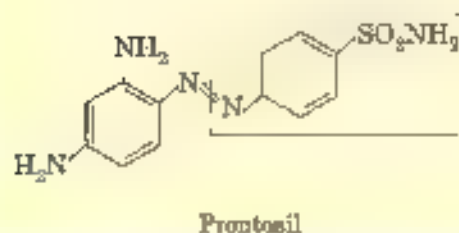
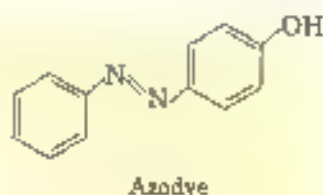
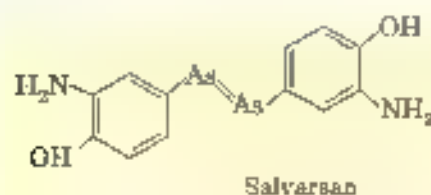
1. by drugs which kill the organism in the body (**bactericidal**),
2. by drugs which inhibit or arrest the growth of the organism (**bacteriostatic**) and
3. by increasing immunity and resistance to infection of the body (**immunity**).

In the early 20th century the scientists tried to search the chemicals that would adversely affect the invading micro-organisms. One such was Paul Ehrlich, a German bacteriologist investigated arsenic based structures in order to produce a drug substance for the treatment of syphilis. He developed a medicine **arsphenamine** (known as **Salvarsan**) as the first effective treatment for syphilis. Ehrlich Paul got Nobel Prize in medicine in 1908 for his discovery. Although **salvarsan** is toxic to human beings but its effect on the bacteria *Spirochete* which causes syphilis is much more than on the human beings and hence it can be used for the treatment. By studying similar structures res

Ehrlich Paul got Nobel Prize in medicine in 1908 for his discovery of **arsphenamine** known as **Salvarsan** for treatment of syphilis.



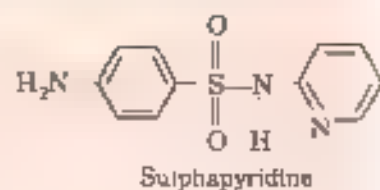
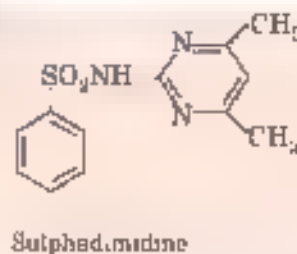
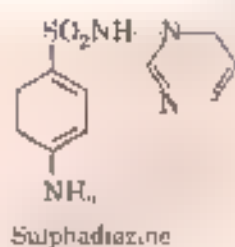
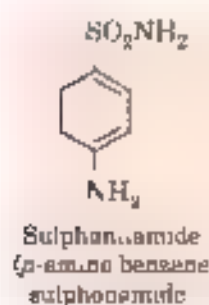
of salvarsan and azodyes in which the linkages $\text{As}=\text{As}$ are similar to $\text{N}=\text{N}$ linkages in azodyes, he observed that tissues are coloured by the dyes selectively. In 1932 he succeeded in preparing the first antibacterial agent known as **prontosil** which resembles in structure to salvarsan.



This led scientists to study the relationship between structure and activity of medicinal compounds. The part of prontosil shown in the box is *p*-amino benzene sulphonamide (sulphanilamide) which showed antibacterial activity.

Antimicrobial substances may be synthetic chemicals like **sulphonamides**, **para-amino salicylic acid** or they may be antibiotics like tetracycline, penicillin, chloramphenicol, etc. (discussed later).

The common example of antimicrobial drug is **sulphanilamides** which are effective in wide range of micro-organisms. These are structural analogues of *p*-amino benzoic acid.



Large number of derivatives of sulphanilamide such as **sulphadiazine**, **sulphadimidine**, **sulphadimethoxine**, **sulphadoxine**, **sulphasomidine** are being used as antimicrobials. One of the most effective is **sulphapyridine**.

Sulphonamides in combination with **trimethoprim** are preferred in the treatment of infections of urinary tract.

7 Antifertility drugs

These are the chemical substances used to control the pregnancy. These are also called **oral contraceptives**. The basic aim of antifertility drugs is to prevent conception or fertilization and therefore these are also known as **birth control pills**.

Oral contraceptives belong to the class of natural products known as **steroids**. These are the active ingredients of the pill functioning as an antifertility agent. These control the female menstrual cycle and ovulation. It is estimated that about 50-60% adult women throughout the world take these pills as the primary form

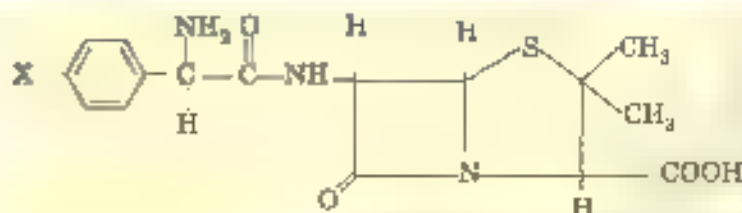
The antibiotics may be either *bactericidal* (kills the organism in the body) or *bacteriostatic* (inhibits the growth of organisms). These are

Bactericidal	Bacteriostatic
Penicillin	Erythromycin
Aminoglycosides (Streptomycin)	Tetracycline
Ofloxacin	Chloramphenicol

The complete range of micro-organisms attacked by an antibiotic is called its spectrum:

Penicillin has a narrow spectrum. These can be used for curing sore throat, gonorrhoea, rheumatic fever, local infections, etc.

Ampicillin and **amoxycillin** are some modifications of penicillin. It may be noted that many patients develop allergy to penicillin. Therefore, it is essential to test the patient for sensitivity allergy to penicillin before it is administered.



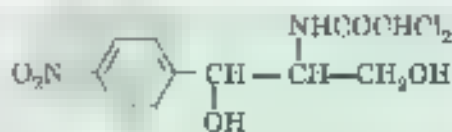
General structure of Penicillin

X = H for ampicillin, X = OH for amoxycillin

In India, the important centres which manufacture Penicillin are Hindustan Antibiotics, Pimpri and Indian Drugs and Pharmaceuticals, Rishikesh and in private sector industry.

Streptomycin and **neomycin** antibiotics are specific for certain diseases such as tuberculosis, meningitis, pneumonia, local infections, etc.

Broad spectrum antibiotics. These are the antibiotics which are effective against several types of harmful micro-organisms. Therefore, these are used for curing a variety of diseases. The common examples are tetracycline, chloramphenicol and chloramphenicol which are effective against a variety of diseases. **Chloramphenicol** is a broad spectrum antibiotic which was isolated in 1947. It is rapidly absorbed from the gastrointestinal tract and hence can be given orally. These can be used for curing typhoid, acute fever, dysentery, whooping cough, pneumonia, eye infections, certain urine infections like meningitis and pneumonia. The structure of chloramphenicol is



Chloramphenicol

Other important broad spectrum antibiotics used are **vancomycin** and **ofloxacin**. The antibiotic **dyadastine** is found to be toxic towards certain strains of cancer cells.

Sulpha drugs. These have great antibacterial powers and are used as medicines for various diseases. These are also antibiotics and protect the body against micro-organisms. These are used against diseases such as

NOTE

The range of bacteria or other microorganisms that are affected by a certain antibiotic is expressed as its **spectrum of action**.

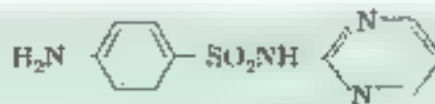
- Antibiotics which kill or inhibit a wide range of gram-positive and gram-negative bacteria are called **broad spectrum antibiotics**.
- The antibiotics which are effective against gram-positive or gram-negative bacteria are called **narrow spectrum antibiotics**.
- The antibiotics which are effective against a single organism or disease are called **limited spectrum antibiotics**.

H W Florey and Alexander Fleming shared their Nobel Prize for medicine in 1945 for their independent contributions to the development of penicillin.

pneumonia, tuberculosis, diphtheria, etc. Some important sulphur drugs are **sulphadiazine**, **sulphathiazole**, **sulphanilamide**, **sulphaguanidine**, **sulphaacetamide**, etc.



Sulphanilamide



Sulphadiazine

9. Antacids

Acidic stomach is necessary for good health, but excessive acidity in the stomach can cause discomforts such as acid indigestion, heart burn, irritation or pain of gastric ulcers.

The chemical substances which neutralize excess acid in the gastric juices and give relief from acid indigestion, acidity, heart burn and gastric ulcers are called antacids.

Thus, antacids remove the excess acid and raise the pH to appropriate level in stomach. **Acid gastritis** is one of the common ailment associated with digestion. It is caused by excess of hydrochloric acid in the gastric juice.

Baking soda (sodium hydrogen carbonate) in water is very common antacid. The bases most widely used in antacids are

- Magnesium hydroxide, $Mg(OH)_2$, magnesium carbonate $MgCO_3$ and magnesium trisilicate. These also act as laxatives.
- Aluminium hydroxide gel, aluminium phosphate, dihydroxy aluminium amino acetate.
- Magnesia oxide MgO is also used as an antacid ingredient since it reacts with water to form magnesium hydroxide $Mg(OH)_2$.

The antacids are available in the form of liquids, gels or tablets. Generally liquid antacids are more effective than tablets because they have great surface area available for interaction and neutralisation of acid.

Until 1970 antacids such as sodium bicarbonate or a mixture of aluminium and magnesium hydroxide have been commonly used for the treatment of acidity.

It may be noted that the treatments of acidity with antacids control only the symptoms and not the cause. Therefore, with these metal salts, the patients cannot be treated easily. In advanced stages ulcers become life threatening and its only treatment is removal of the affected part of the stomach.

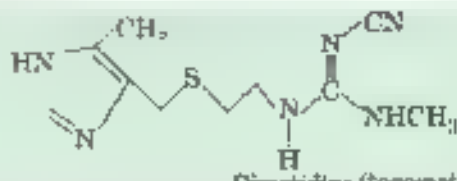
Some sodium salt antacids may cause hypertension because of increase in sodium ions concentration. Therefore the excessive use of these antacids containing sodium ions is not recommended for patients having high blood pressure.

It may be noted that the excessive use of hydrogencarbonate can make the stomach alkaline and trigger the production of even more acid. Metal hydroxides are better alternatives because of being insoluble. These do not increase the pH above neutrality.

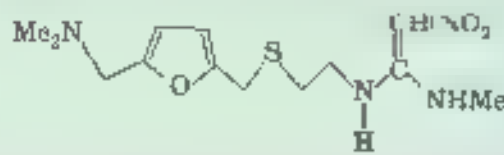
A major advancement in the treatment of hyperacidity came through the discovery that histamine stimulates the secretion of pepsin and hydrochloric acid. To prevent the interaction of histamine with the receptors present in the stomach wall, the drug **cimetidine** (also called **tegamet**) has been designed. This resulted in release of lesser amount of acid. This drug has been replaced by another drug **ranitidine** (Zantac) and is used to even heal peptic ulcers.



Histamine



Cimetidine (tegamet)



Ranitidine (Zantac)

A new class of drugs **omeprazole** and **lansoprazole** are most effective drugs which prevent the formation of acid in the stomach.

It may be noted that milk is a weak antacid which also possesses a protective action.

10. Antihistamines

A number of different sensitising substances (called antigens, derived from food or environment may cause allergic reactions in human beings. This is due to the release of a chemical substance called **histamine** in the body.

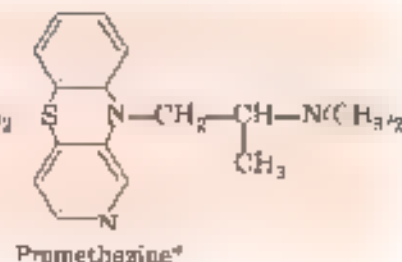
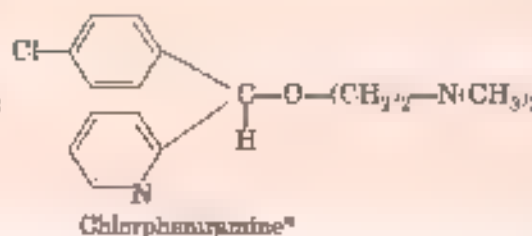
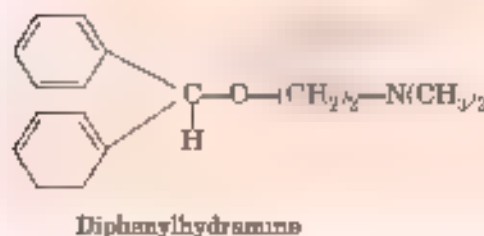
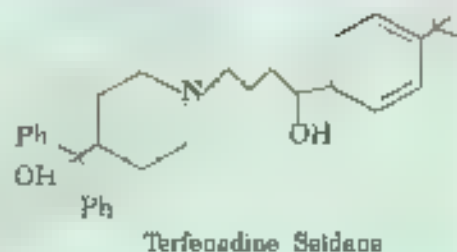
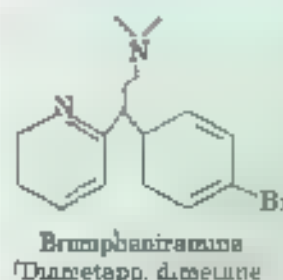
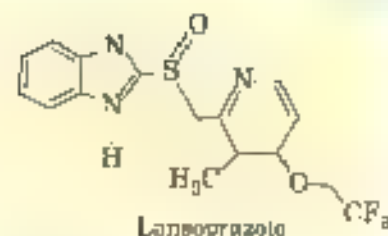
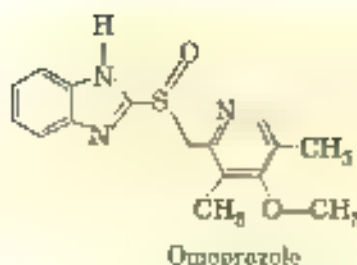
Histamine is a potent vasodilator and performs various functions. For example, histamine contracts the smooth muscles in the bronchi and gut (to which patients of asthma are very sensitive) and relaxes other muscles such as those in the walls of fine blood vessels. Histamine is also responsible for the nasal congestion associated with common colds, cough, allergic response to pollens, etc.

Antihistamines are chemical substances which diminish or abolish the main actions of histamine released in the body and hence prevent the allergic reactions.

Symmetrical drugs such as **brompheniramine** (Dimetapp) and **terfenadine** (seldane) are used as antihistamines. They interfere with the natural action of histamine by competing with histamine for binding sites of receptor where histamine exerts its effect.

Antihistamines are also called **antiallergic drugs**. These are used to treat allergy e.g. skin rashes. Other allergic reactions are conjunctivitis, inflammation of conjunctiva of eye and rhinitis, inflammation of nasal mucosa. In seasonal rhinitis and conjunctivitis, these drugs relieve sneezing, nasal discharge and asthma, itching of eyes, nose and throat.

The common antihistamine drugs are **diphenyl hydramine** (Benadryl), **pheniramine maleate** (Aviol), **chlorpheniramine** (Zeel), **promethazine**, **triprolidine** (actidil), **antazoline** (antistine), **dimethindene** (forista).



11. Anaesthetics

These are the chemical substances which produce general or local insensibility to pains and other sensations. Cocaine and novocaine are local anaesthetics. Chloroform, diethyl and vinyl ethers, etc. are general anaesthetics.

Chemicals in medicines

Chemicals in medicines

• Anaesthetics	: Relieve pain	Aspirin, ibuprofen, diclofenac sodium, naproxen, narcotics (morphine, codeine, heroin)
• Antipyretics	: Lower body temperature	Aspirin, paracetamol, phenacetin
• Antiseptics and disinfectants	: Kill or prevent the growth of micro-organisms	0.2% phenol antiseptic, 1% phenol disinfectant, chlorate, dettol (chloroxylenol) and cerpureol (bitartronic acid, iodine, sorbic acid)
• Tranquilizers	: Treatment of stress, mental changes	Derivatives of barbituric acid: veronal, amytal, methohel, luminal, seconal, chloridiazepoxide, meprobamate, valium, serutinon.
• Antimicrobials	: Cure infectious due to micro-organisms microbes	Antibiotics, sulphonamides
• Antifertility drugs	: Birth control	Oral contraceptives: oestrogen ethinylmestranol and progesterone norethandrone, mifepristone
• Antibiotics	: Produced by micro-organisms and can inhibit the growth of other micro-organisms	Penicillin, tetracycline, chloramphenicol, ampicillin, amoxycillin Sulpha drugs: sulphamamide, sulphadiazine, sulphaguanidine
• Antacids	: Remove excess acid in stomach	Magnesium carbonate, magnesium carbonate, magnesium trisilicate, aluminium hydroxide gel, sodium bicarbonate, aluminium phosphate, ranitidine, lansoprazole

add on

Conceptual Questions

1

Q.1. (a) Why is bithional added to soap?

(b) Which class of drugs is used in sleeping pills?

(D.S.B. 2013, A.I.S.B. 2013)

Ans. (a) Bithional acts as an antiseptic agent and reduces the odours produced by the bacterial decomposition of organic matter on the skin.

(b) Tranquilizers

Q.2. (i) What class of drug is Ranitidine?

(ii) Which of the following is an antiseptic?

0.2% phenol, 1% phenol /

(A.I.S.B. 2013)

Ans. (i) Antacid

(ii) 0.2% phenol antiseptic, 1% phenol disinfectant

Q.3. Pick out the odd one from among the following compounds on the basis of their medicinal properties mentioning the reasons.

Luminal, seconal, phenacetin, equanil.

Ans. Phenacetin

Q.4. Pick out the odd one out from among the following on the basis of their medicinal properties mentioning the reason.

Chloroxylenol, phenol, chloramphenicol, bithional.

Ans. Chloramphenicol

Q.5. Name a broad spectrum antibiotic and two diseases for which it is prescribed.

(Hr. S.B. 2013, H.P.S.B. 2013, Jammu S.B. 2013)

Ans. Chloramphenicol is a broad spectrum antibiotic.

It is prescribed for curing (i) typhoid (ii) dysentery

Q.6. Which chemical is responsible for the antiseptic properties of dettol ?

(CBSE Sample Paper 2012, Assam S.B. 2012)

Ans. Chloroxylenol

Q.7. Name a substance which can be used as an antiseptic as well as disinfectant.

(H.P.S.B. 2017)

Ans. Phenol

Q.8. Name the class of antimicrobial drugs.

Ans. Sulphonamides

Q.9. Name the most common antacid.

Ans. Baking soda

Q.10. What are antibiotics ? Name the first antibiotic discovered ?

(Meghalaya S.B. 2013)

Ans. Antibiotics are chemical substances which are produced by micro-organisms bacteria, fungi and moulds and can inhibit the growth or even destroy other micro organisms.

Penicillin was the first antibiotic discovered

Q.11. What type of drug is phenacetin ?

(Hr. S.B. 2018)

Ans. It is analgesic

Q.12. Give an example of a sulphur drug.

(Ph.S.B. 2002, Assam S.B. 2018)

Ans. Sulphadiazine

Q.13. A pain reliever used for relief from severe pain like post-operative pain or pain due to terminal cancer.

(CBSE Sample Paper 2011)

Ans. Morphine

Q.14. Name one substance which can act as both :

(i) Analgesic and antipyretic. (CBSE Sample Paper 2012, Assam S.B. 2012, Hr. S.B. 2012, Pb. S.B. 2018)

(ii) Antiseptic and disinfectant.

(CBSE Sample Paper 2011, Pb. S.B. 2013)

Ans. (i) Aspirin (ii) Phenol

Q.15. What are the main constituents of dettol ?

(D.S.B. 2011)

Ans. The main constituents of dettol are chloroxylenol and terpineol in a suitable solvent.

Q.16. What is tincture of iodine and what is it used for ?

(Pb. S.B. 2013, Assam S.B. 2013, H.P.S.B. 2013, A.I.S.B. 2011, 2018)

Ans. 2-3% iodine solution of alcohol-water is called tincture of iodine. It is a powerful antiseptic and is applied on wounds.

Q.17. Giving one example of each analgesics and tranquilizers.

(Uttarakhand S.B. 2018)

Ans. Aspirin, morphine

Q.18. Sleeping pills are recommended to patient suffering from sleeplessness but it is not advisable to take them without consulting the doctor. Why?

(Assam S.B. 2013)

Ans. Most of the drugs taken in doses higher than recommended dose may cause harmful effects and act as poison leading to death. Therefore a doctor must always be consulted before taking any medicine. who will advice the patient for proper and safe doses of the drug.

Q.19. Name first antibiotic.

(H.P.S.B. 2013)

Ans. Penicillin

Q.20. Name the medicine which reduces fever.

(Hr. S.B. 2013)

Ans. Antipyretics e.g. paracetamol

Q.21. Give the name of one neurotransmitter.

(Meghalaya S.B. 2013)

Ans. Acetylcholine

CHEMICALS IN FOOD

Many chemicals are added to food for their preservation and enhancing their appearance. These are called food additives and are

- (i) Flavours and sweeteners
- (ii) Food colours dyes.
- (iii) Fat emulsifiers and stabilising agents
- (iv) Flour improvers antistaling agents and bleaches

(v) Antioxidants

(vi) Preservatives

(vii) Nutritional supplements such as vitamins, minerals and amino acids.

Except for nutritional supplements, all other do not have nutritive value. These are added to increase the self life of the stored food or for cosmetic purposes. Antioxidants, preservatives, fat emulsifiers and staining agents as well as flour improvers are used to increase the self life of the stored food while dyes, flavours and sweetening agents help to improve their cosmetic value. Some of these are discussed below.

1. Food preservatives

These are the chemical substances which are added to the food materials to prevent or retard their spoilage and to retain their nutritive value for long periods.

These preservatives prevent the rancidity of food and inhibit the growth or kill the micro-organisms. The common salt, sugar, oils and spices provide a medium that resists the activity of micro-organisms in food. The preservation of food by adding sufficient amount of salt to it is called **salting**. It is used for the preservation of raw mungo, or lent, beans, tamarind, fish, meat, etc. The salt prevents the water from being available for microbial growth.

Sugar syrup is used for preserving many fruits such as apples, mango, strawberry, carrot, etc.

Besides sugar and salts, other substances such as vinegar, oils, spices, citric acid are also used as food preservatives, which are used for pickles, ketchups, jams, squashes, etc.

The growth of microbes in food materials can also be prevented by adding certain chemical substances.

Sodium benzoate (C_6H_5COONa) is the most commonly used preservative. It can be used safely in limited amounts and is metabolized by conversion to hippuric acid $C_6H_5CONHCH_2COOH$, which is ultimately excreted in the urine.

Salts of propionic acid and sorbic acid are used as preservatives for controlling the growth of yeasts and moulds in food items such as cheese, pickles, baked food, certain meat and fish products.

Sodium or potassium metabisulphites (source of sulphur dioxide) are used as preservatives for jams, squashes, pickles, etc.

Certain food preservatives such as butylated hydroxyanisole (BHA) and butylated hydroxy toluene (BHT) for edible oils also act as antioxidants. Salts of sorbic acid and propanoic acid are also used as preservatives.

2. Antioxidants

Fats and oils, and the foods containing fats and oils are readily oxidised, they turn rancid and their smell and taste change. As a result of rancidity they become unpalatable. Usually substances which prevent oxidation of foods containing fats and oils are added and these substances are called antioxidants. Thus,

antioxidants are substances which prevent or retard the oxidative deterioration of food.

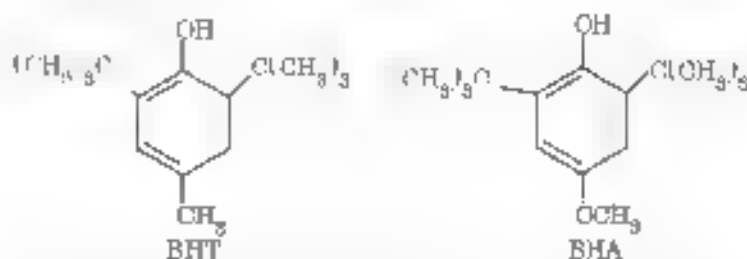
The antioxidants act as sacrificial materials because they are more reactive towards oxidation than the food materials. These antioxidants also minimise the damage to some amino acids and the loss of some vitamins due to rancidity. During oxidation of food, free radicals are generated. The antioxidants react

The preservative action of sodium or potassium metabisulphites ($Na_2S_2O_4$ or $K_2S_2O_4$) is due to SO_2 which dissolves in water to form sulphurous acid, H_2SO_3 .



Sulphurous acid inhibits the growth of yeasts, moulds and bacteria. Instead of $Na_2S_2O_4$, SO_2 itself can be used as preservative for fresh vegetables and fruits.

with these free radicals and stop the chain reaction of oxidation of the food. Thus, antioxidants decrease the rate of involvement of free radicals in the aging process. The most common antioxidants are **butylated hydroxy toluene (BHT)** and **butylated hydroxy anisole (BHA)**.



These phenolic compounds are added to preserve fats in packaged food. Oxygen reacts preferentially with BHA or BHT rather than oxidising fats or oils and therefore, these prevent oxidative spoilage of food items.

Sometimes BHA and BHT are added to food items in combination with citric acid or ascorbic acid to produce a more active synergistic effect.

Sulphur dioxide and sulphite are also used as antioxidants for their technological efficiency and versatility. They are active as antimicrobials, agents, structure modifiers, antioxidants and enzyme inhibitors. The salts used are sodium or potassium sulphites and bisulphites. They are commonly used in wine and beers, fruit juices, pickles, sugar syrups and cut peeled or dried fruits and vegetables.

8. Artificial Sweetening Agents

These are the chemical compounds which give sweetening effect to the food and enhance its odour and flavour.

Natural sweetening agents such as sucrose, **maltose** (milk sugar), cane syrup, honey are most widely used. However, the **addition** to our calorie intake and therefore, many people prefer to use artificial sweeteners. Some important artificial sweeteners are:

Saccharin ortho-sulphobenzimide is the first most popular artificial sweetening agent. It has been used as a sweetening agent for many articles of food ever since its discovery in 1879. It is 1,2-benzisothiazolin-3-one-1,1-dioxide and occurs as white crystalline powder. It has very sweet taste and is about 500 times more sweet than sucrose. It is excreted from the body in urine unchanged. It appears to be entirely inert and harmless when taken. Its use is of **great value to diabetic persons and people who need to control intake of calories**.

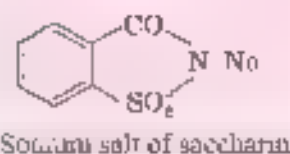
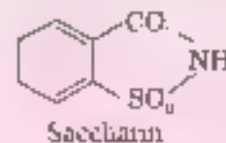
Sodium salt of saccharin is water soluble salt which is more palatable and free from unpleasant after taste of saccharin. It is the dihydrate of the sodium salt of saccharin. Its calcium salt is also water soluble and is used.

Aspartame, It is one of the most widely used artificial sweetener. It is methyl ester of dipeptide derived from aspartic acid and phenylalanine. It is about 100 times as sweet as sucrose. It may be noted that aspartame is unstable at cooking temperatures and therefore, it is used as **sugar substitute to cold foods and soft drinks**.

(ii) **Alitame**, It is a high potency sweetener and is more stable than aspartame during cooking. However, there is one main difficulty with alitame and similar type of high potency sweeteners that it is difficult to control the sweetness of the food to which they are added.

(iii) **Sucralose**, It is trichloroderivative of sucrose. Its appearance and taste are similar to sugar and is stable at cooking temperature. It does not provide calories.

Ascorbic acid (vitamin C) and tocopherols (vitamin E) have also been used as antioxidants.



Saccharin and its salts have been proved to be safe even for countless diabetics and is of great value to people who need to control intake of calories.

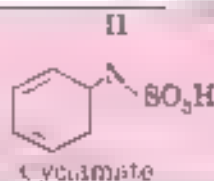
These artificial sweetening agents are constituted from compounds that mimic the effects of sugar on the tongue but do not undergo the metabolic reactions in the body. In other words, they pass through the human body without being metabolised, without producing any calories. Aspartame is an exception, because the body breaks it down into naturally occurring amino acids and methanol and absorbs these as usual. Therefore, *these artificial sweeteners* are called **low calorie sweeteners or calorie-free sweeteners**. A polyhydric compound, xylitol, is used as a sweetener in sugarless gum.

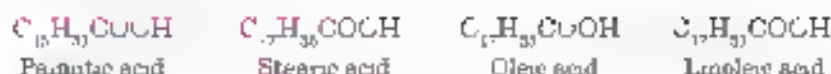
Artificial sweetener	Structural formula	Sweetness value in comparison to cane sugar
Aspartame	<p>from aspartic acid</p> <p>from phenylalanine methyl ester</p>	100
Dulcin		300
Sucralose		600
Aluminate		2000

In recent years, there has been a great search for a safe, calorie free sweeteners to help diabetes who want to control sugar intake. **Calcium cyclamate** was used as calorie free sweetener. However its use was banned in United States because of a suspected link with cancer. Sucralose is expected to become a great commercial sweetening agent.

CLEANSING AGENTS

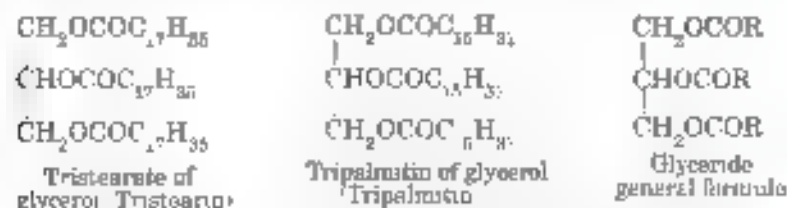
Soaps and detergents are substances which are used for cleaning. Soaps are very popular cleansing agents which have been used for more than two thousand years. The soaps are sodium or potassium salts of higher fatty acids containing long chains of 12 to 18 carbon atoms. The common examples of higher fatty acids used for making soaps are



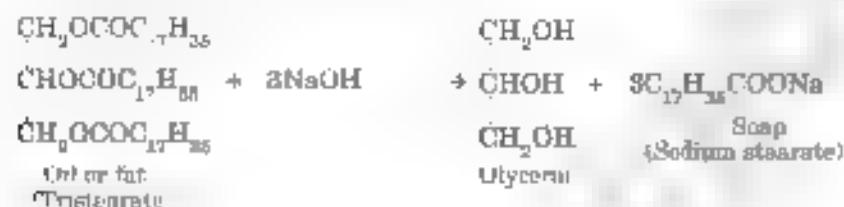


Sodium or potassium salts of these higher fatty acids are soaps. For example sodium palmitate, sodium stearate, sodium oleate, etc.

Soaps are made from animal fats or vegetable oils. Fats and oils are esters of higher fatty acids and glycerol. The esters of glycerol and higher fatty acids are called **glycerides**. For example, the tristearate of glycerol is called tristearin; a tripalmitate of glycerol is called tripalmitin.



When oils and fats (glycerides) are heated with a solution of sodium hydroxide they break down to sodium salt of the respective fatty acid (soap) and glycerol. This process of making soap by the hydrolysis of fats and oils with alkalis is called **saponification**.



The soap is separated from the solution by the addition of common salt ($NaCl$). Salt is added to decrease the solubility of soap and it helps to precipitate out or salt out from the aqueous solution. Soap is lighter than water and it floats on the surface from where it is removed. The solution remaining behind contains glycerol and sodium chloride. Glycerol is recovered from the solution as it is very useful chemical used in drugs, cosmetics, explosives and paints.

Soap is mixed with desired colours, perfumes and chemicals of medicinal importance e.g. in neem soap, carbolic soap, etc. It is then cast into desired shape for use.

Types of Soaps

All soaps are made by heating fats and oils with suitable soluble hydroxide. Variations are made by using different raw materials. In general, sodium soaps are hard whereas potassium soaps are soft. Some important types of soaps are:

(i) **Toilet soaps.** These are prepared by using better grades of oils and fats and care is taken to remove excess alkali. Therefore, these soaps are normally free from excess alkali and form more lather. Colours or perfumes are added to make them more attractive.

(ii) **Medicated soaps.** These soaps are the soft soaps containing substances of medicinal value. In some soaps deodorants are added. Neem soap, carbolic soaps are some common examples of medicated soaps.

(iii) **Shaving soaps.** These soaps are potassium sodium stearates and produce a strong lather. These contain glycerol to prevent rapid drying. A gum called rosin is added in these soaps which forms sodium rosinates which lathers well.

Like D-sugars, L-sugars are also sweet in taste but do not provide energy because our body does not have enzymes for their metabolism. Therefore, these are secreted out such from our body through urine. So these L-sugars (L-glucose, L-galactose, etc.) have been synthesised and can be used as artificial sweetening agents.

(vi) **Laundry soaps.** These soaps contain fillers like soda ash, carbonate, sodium silicate, borax and sodium carbonate.

(vii) **Transparent soaps.** These soaps are prepared by dissolving the soap in ethanol and then evaporating the excess solvent.

(viii) **Floating soaps.** These soaps float in water and are prepared by beating tiny air bubbles into the product before it hardens.

(ix) **Soap chips.** These are prepared by running a thin sheet of melted soap into a cool cylinder and scraping off the soaps in small, broken pieces.

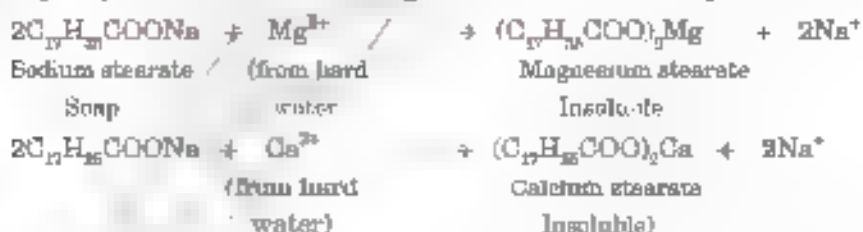
(x) **Soap granules.** These are dried miniature soap bubbles.

(xi) **Soap powder and scouring soaps.** These substances contain some soap, a scouring agent, a abrasive such as powdered pumice or finely divided sand and binders like sodium carbonate and trisodium phosphate. Binders help the soaps to act more quickly.

Soaps as Cleansing Agents

Soap is a good cleansing agent and is 100% biodegradable i.e. micro-organisms present in sewage water can completely oxidise soap. Therefore, soaps do not cause any pollution problems. However, soaps have two serious limitations.

1. Soaps cannot be used in hard water. Hard water contains certain metal ion, such as Ca^{2+} and Mg^{2+} . These ions react with soap to form a curdy white precipitate of calcium and magnesium salts. For example,



These precipitates stick to the fibres of the cloth as gummy mass and blocks the ability of soaps to remove oil and grease from fabrics. Therefore, it interferes with the cleansing ability of the soap and makes the cleansing process difficult. Hair washed with hard water look dull because of this sticky precipitate. Dyes do not absorb evenly on cloth washed with soap and using hard water because of this gummy mass.

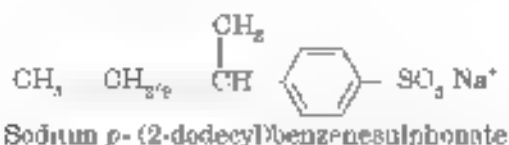
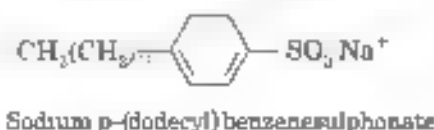
2. Soaps cannot be used in acidic medium. In acidic medium, the acids present in solution precipitate the insoluble free fatty acids which adhere to the fabrics and hence block the ability of soaps to remove oil and grease from the fabrics.

Synthetic Detergents or Soapless Soaps

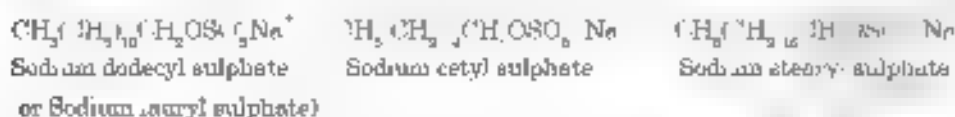
To overcome this difficulty, synthetic detergents have been prepared. These synthetic detergents have structures similar to soaps. These are also called **soapless soaps** because though they behave like soaps, not having cleaning properties yet they do not contain the usual soaps like sodium salts of fatty acids. These are better cleansing agents because they do not form insoluble calcium and magnesium salts with hard water. Therefore, they can be used even in hard water because they give foam in the water containing mineral compounds. Some of these synthetic detergents give foam even in ice cold water.

These are manufactured chemically from materials other than animal fats. For example, these are obtained from alkyl benzene sulphonates and alkyl hydrogen sulphates. Therefore, synthetic detergents are sodium salts of long chain sulphonates and sulphates. Therefore, these are of two types

(i) **Sodium salts of long chain alkylbenzene sulphonic acid.** These are obtained from derivatives of benzene sulphonic acid. The common examples are sodium *p*-(dodecyl) benzenesulphonate and sodium *p*-(2-dodecyl) benzene sulphonate.



(ii) **Sodium salts of long chain alkyl hydrogen sulphate.** These are sodium salts of sulphuric acid esters of long chain alcohols containing usually 10-15 carbon atoms. These alcohols are obtained by the hydrogenolysis of oils and fats. For example, sodium dodecyl sulphate or sodium lauryl sulphate, sodium cetyl sulphate and sodium stearyl sulphate.



Unlike ordinary soaps, these do not produce hydroxy ions on hydrolysis and therefore, can be safely used for woollen garments.

CLASSIFICATION OF DETERGENTS

Depending upon the nature of surface active group, detergents may be classified as

1. Anionic or cationic or non-ionic

(i) Anionic detergents

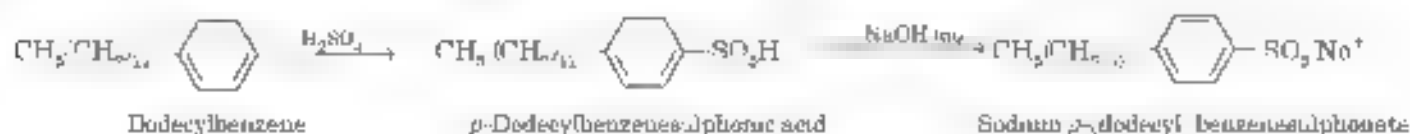
The anionic detergents are those which contain an anionic hydrophobic group which is involved in cleansing action. These are sodium salts of sulphonated long chain alcohols or hydrocarbons. These detergents are of two types

(a) **Sodium alkyl sulphates.** These are obtained from long chain alcohols containing 12-18 carbon atoms. The long chain alcohols are treated with concentrated sulphuric acid to form alkyl hydrogen sulphates of high molecular mass and then these are neutralised with alkali to form salt.

The common examples of this type of detergents are sodium lauryl sulphate $\text{C}_{12}\text{H}_{25}\text{CH}_2\text{OSO}_3\text{Na}^+$ and sodium stearyl sulphate, $\text{C}_{17}\text{H}_{35}\text{CH}_2\text{OSO}_3\text{Na}^+$. For example,



(ii) **Sodium alkyl benzene sulphonates.** These are sodium salts of long chain alkyl sulphonic acids. For example, sodium *p*-(dodecyl) benzene sulphonate is prepared by treating dodecyl benzene with concentrated H_2SO_4 to form *p*-dodecyl benzene sulphonic acid followed by neutralisation with NaOH.



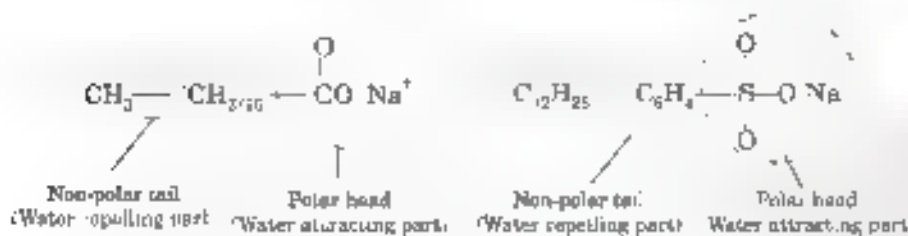
Cleansing action of soaps and detergents

The cleansing action of soaps and detergents follows the same principle. Soaps and detergents consist of two parts

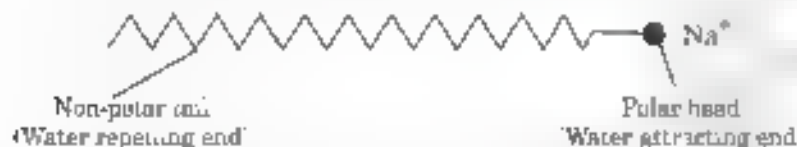
→ A non-polar part which consists of long chain hydrocarbon part. It is called non-polar tail. This part is insoluble in water but soluble in oil and grease. This is also called **water repelling** or **hydrophobic part**.

→ An ionic part which consists of carboxylate ion (in case of soaps) or a diphenates or sulphates in case of detergents. This is called **polar head**. It is soluble in water but insoluble in oil or grease. The ionic part is called **water attracting** or **hydrophilic part**.

These two parts of soaps and detergents may be represented as



For simplicity, soaps and detergents may be represented as

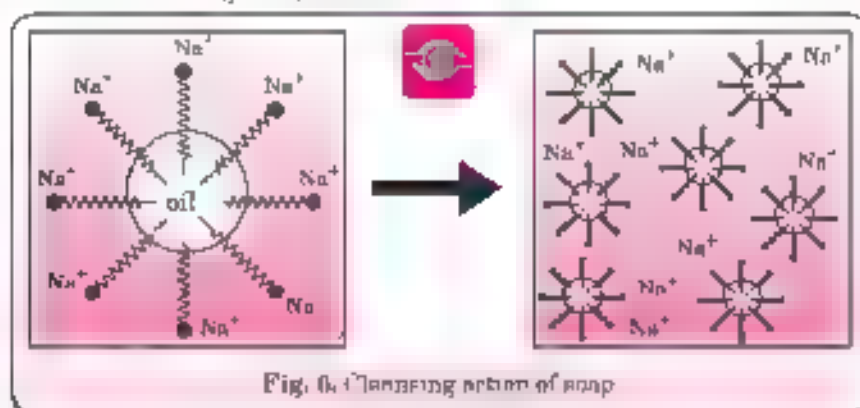


Therefore, soaps and detergents consist of a large hydrocarbon tail with negatively charged head. The hydrocarbon tail is hydrophobic (water repelling) and negatively charged head is hydrophilic (water attracting).

The dirt in the cloth is due to the presence of dust particles in fat or grease which stick to the cloth. When a soap or a detergent is dissolved in water, the molecules gather together as clusters called **micelles**. When the dirty cloth is dipped in soap or detergent solution, the soap and dust particles come in contact with each other. The non-polar tails of the soap begin to dissolve in non-polar oil or grease, while the polar head part remains directed in water. Fig. 6. As more and more soap particles enter the grease, each fat or oil particles is surrounded by a number of negatively charged ends. Since the **similar** charges repel each other, the oil or grease droplets break off into small globules of oil. These are still surrounded by the negatively charged polar heads of the soap molecules. This prevents the small globules from coming together to form bigger particles (aggregates). The rubbing by hands or mechanical stirring also help to break the grease particles. In this manner the grease particles can be completely broken up and it forms emulsion of grease or oil contained in dirt and water. As a result, the cloth gets free from the dirt and the droplets are washed away with water.

Therefore, they tend to remain in water bodies for a long time and make water unfit for aquatic life. For example, detergents containing phosphates can cause rapid growth of algae and therefore, deplete the dissolved oxygen present in the water of lakes and rivers. As a result of lack of oxygen fish and other aquatic animals may die.

To solve these problems, nowadays, the detergents are prepared from hydrocarbons which have minimum branching. These are degraded more easily than branched chain detergents. Therefore, these are **biodegradable** and pose less problems.



Differences between Soaps and Detergents

The main points of differences between soaps and detergents are given below

Soaps	Synthetic Detergents
<ul style="list-style-type: none"> Soaps are sodium salts of long chain fatty acids. They cannot be used in acidic solutions. They cannot be used in hard water as they produce precipitates with Ca^{2+} and Mg^{2+} ions. Soaps are biodegradable. Therefore, they do not cause any pollution problems. 	<ul style="list-style-type: none"> Synthetic detergents are sodium salts of long chain alkyl sulphates or long chain alkyl benzene sulphonates. They can be used even in acidic solutions. They can be used even in hard water as they do not form any precipitates with Ca^{2+} or Mg^{2+} ions. Some of the synthetic detergents are not biodegradable. Therefore, they pollute river and lake water.

Advantages of Synthetic Detergents over Soaps

Synthetic detergents are widely used as cleansing agents these days. Some of their advantages over soaps are

(i) Synthetic detergents can be used for washing even in hard water. On the other hand, soaps are not suitable for use with hard water.

(ii) Synthetic detergents can be used even in acidic solutions because they are not readily decomposed in acidic medium. On the other hand, soaps can not be used in acidic medium because they are decomposed into carboxylic acid in acidic medium.

(iii) Synthetic detergents are more soluble in water than soaps.

(iv) Synthetic detergents have a stronger cleansing action than soaps.

(v) Some synthetic detergents give foams even in ice cold water.

add on

Conceptual Questions

Q.1 (a) Which one of the following is a food preservative?

Equanil, Morphine, Sodium benzoate.

(D.S.B. 2018)

(b) If water contains dissolved Ca^{2+} ions, out of soaps and synthetic detergent, which will you use for cleaning clothes?

(A.I.S.B. 2019)

Ans. (a) Sodium benzoate (b) Synthetic detergent

Q.2. Name one synthetic sweetening agent.

(Hr. S.B. 2018)

Ans. Saccharin

Q.3. Give one example of a non-ionic detergent.

Ans. $\text{CH}_3(\text{CH}_2)_{15}\text{COO}(\text{CH}_2\text{CH}_2\text{O})_5\text{CH}_2\text{CH}_2\text{OH}$

Q.4. Give the structure of an alkyl benzene sulphonate detergent.

(D.S.B. 2009)

Ans. Sodium *p*-dodecyl benzene sulphonate



Q.5. What is BHA and BHT ?

(Pb. S.B. 2005)

Ans. BHA is butylated hydroxy anisole
BHT is butylated hydroxy toluene
Both are used as antioxidants in food.

Q.6. What are the consequences of using non-biodegradable detergents ?

(Pb. S.B. 2005)

Ans. Non-biodegradable detergents are degraded very slowly by micro-organisms. Therefore, they get accumulated in rivers and water ways causing water pollution.

Q.7 Why the detergents with straight hydrocarbon groups are better than the detergents with branched chain hydrocarbon groups ?

(Hr. S.B. 2006)


Ans. The detergents with straight chain hydrocarbon group are more biodegradable than detergents with branched chain hydrocarbons. Therefore, detergents with straight chain hydrocarbons are easily decomposed or broken down by micro-organisms like bacteria present in water bodies. Therefore, they cause less water pollution and hence are better.

Q.8. Name two artificial sweeteners used in food materials.

Ans. (i) Aspartame (ii) Alitame

Q.9. Give one example each of cationic and anionic detergent.

Ans. Cationic detergent $\left[\begin{array}{c} \text{CH}_3 \\ \text{CH}_3 \text{CH}_2 \text{---} \text{N}^+ \text{---} \text{CH}_3 \\ \text{CH}_3 \end{array} \right] \text{Cl}^-$ Tetramethyl ammonium chloride

Anionic detergent : $\text{C}_{12}\text{H}_{25}$ —— SO_3^-Na^+ Sodium p-dodecyl benzene sulphonate

Q.10. Name the sweetening agent used in the preparation of sweets for a diabetic patient.

(H.P. S.B. 2013)

Ans. Aspartame or saccharin

Q.11 Why do we require artificial sweetening agents?

(CBSE Sample Paper 2011)

Ans. Artificial sweetening agents are required as natural calorie intake and as a substitute of sugar for diabetes.

Q.12. Give one example for each of the following

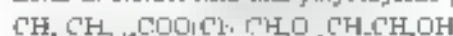
(i) An artificial sweetener whose use is limited to cold drinks.

(ii) A non-ionic detergent.

(CBSE Sample Paper 2011)

Ans. (i) Aspartame.

(ii) Ester of stearic acid and polyethylene glycol



Q.13. Among the following which one acts as a food preservative?

Asparagine, Aspirin, Sodium benzoate, Paracetamol

(A.I.S.B. 2018)

Ans. Sodium benzoate

Key Terms & Laws

- **Medicines or drugs.** The chemicals used for treatment of diseases and reducing sufferings and pain.
- **Agonist.** A drug which stimulates or activates the receptor to initiate a physiological response is called agonist.
- **Antagonist.** A drug which occupies the receptor site without producing any response is called antagonist.

QUICK CHAPTER ROUND UP

Chemicals in Medicine

• Analgesics	Relieve pain	Aspirin, ibuprofen, diclofenac sodium, naproxen, narcotics morphine, codeine, heroin
• Antipyretics	Lower body temperature	Aspirin, paracetamol, phenacetin
• Antiseptics	Kill or prevent the growth of microorganisms (not harmful for living tissues)	Phenol, chloramine, dettol, chloroxylenol and terpineol, 0.2% phenol
• Disinfectants	Kill or prevent the growth of microorganisms (harmful for living tissues and can be used on non-living objects, clothes, floors, utensils etc)	1% phenol, I_2 , cresols
<p>• The same substance acts as disinfectant and antiseptic e.g., 0.5% phenol is antiseptic and 1% phenol is disinfectant</p>		
• Tranquilizers	Treatment of stress, mental diseases	Derivatives of barbituric acid, veronal, amytal, amital, secobarbital, chloralhydrate, m-probamate, valium, serotonin
• Antimicrobials	Cure infections due to microorganisms (microbes)	Antibiotics, sulphonamides
• Antifertility drugs	Birth control	Oral contraceptives, estrogen, ethinyl estradiol and progesterone, norethindrone, norgestrel
• Antibiotics	Produced by microorganisms and can inhibit the growth of other microorganisms	Penicillin, streptomycin, chloramphenicol, ampicillin, amoxycillin, cephalosporins, sulphamonomide, sulphadiazine, rifampicin, rifamides
<p>• Penicillin G has a narrow spectrum • Ampicillin and amoxycillin are its synthetic modifications • Chloramphenicol is a broad spectrum antibiotic</p>		
• Antihistamines	Anti-allergy	Diphenhydramine, benadryl, brompheniramine, clemastine, pheniramine maleate (avil), chlorpheniramine maleate (cetir)
• Antacids	Remove excess acid in stomach	Magnesium hydroxide, magnesium carbonate, magnesium trisilicate, aluminum hydroxide gel, sodium bicarbonate, aluminum phosphate, ranitidine, famotidine

Chemicals in Food

<ul style="list-style-type: none">• Food preservatives Aided to food materials to prevent or retard their spoilage• Common salt• Sodium benzoate• Sodium metabisulphite• BHA and BHT act as antioxidants	<ul style="list-style-type: none">• Artificial sweetening agents give sweetening effect to food and enhance its odour and colour <table><thead><tr><th>Artificial sweetener</th><th>Sweetness value comparison to cane sugar</th></tr></thead><tbody><tr><td>➤ Aspartame</td><td>100</td></tr><tr><td>➤ Saccharin</td><td>550</td></tr><tr><td>➤ Sucralose</td><td>800</td></tr><tr><td>➤ Alulose</td><td>2000</td></tr></tbody></table> <p>⇒ Use of aspartame is limited to cold foods and soft drinks</p>	Artificial sweetener	Sweetness value comparison to cane sugar	➤ Aspartame	100	➤ Saccharin	550	➤ Sucralose	800	➤ Alulose	2000	<ul style="list-style-type: none">• Antioxidants Prevent or retard the oxidation and subsequent spoilage of food• BHA Butylated hydroxy anisole• BHT Butylated hydroxy toluene• SO₂ and sulphates
Artificial sweetener	Sweetness value comparison to cane sugar											
➤ Aspartame	100											
➤ Saccharin	550											
➤ Sucralose	800											
➤ Alulose	2000											

Cleaning Agents

• Soaps are acid with or potassium salts of higher fatty acids (16-18 C atoms e.g. salts of $\text{C}_{17}\text{H}_{35}\text{O}_2$ - palmitic acid, $\text{C}_{18}\text{H}_{37}\text{O}_2$ - stearic acid, $\text{C}_{19}\text{H}_{39}\text{O}_2$ - oleic acid, $\text{C}_{20}\text{H}_{41}\text{O}_2$ - lauric acid)	• Synthetic detergents are sodium salts of long chain alkyl hydrogen sulphates or long chain benzene sulphonic acids.
	$\text{CH}_3(\text{CH}_2)_{11}\text{CH}_2\text{OSO}_3\text{Na}^+$ Sodium dodecyl sulphate $\text{C}_6\text{H}_5(\text{CH}_2)_{10}\text{CH}_2\text{OSO}_3\text{Na}^+$ Sodium cetyl sulphate $\text{CH}_3(\text{CH}_2)_{11}\text{C}_6\text{H}_4\text{SO}_3\text{Na}^+$ Sodium p-(dodecyl) benzene sulphate



NCERT

Textbook Exercises

Q.1. Why do we need to classify drugs in different ways?

Ans. There are a large variety of drugs for different purposes of diagnosis, prevention, relief or cure of different diseases. These have been classified according to various criteria depending upon their pharmacological effect, upon their action on a particular biochemical process, on the basis of their chemical structure, on the basis of molecular targets, etc. These classification have their own usefulness. For example,

- Classification on the basis of pharmacological effect of the drugs is useful to doctors because it provides them the whole range of drugs available for the treatment of a particular type of disease.
- Classification on the basis of action of a particular biochemical process is useful for selecting the correct lead compound for designing the synthesis of a desired drug.
- Classification on the basis of chemical structure helps to design the drugs having similar pharmacological activity and then selecting the drug with least toxicity.
- Classification on the basis of molecular targets is useful for medicinal chemists so that they can design a drug which is most effective for a particular receptor site.

Q.2. Explain the term "target molecules or drug targets" as used in medicinal chemistry.

Ans. Drugs taken by a patient interact with macromolecules such as proteins, carbohydrates, lipids and nucleic acids and these are called drug targets. These macromolecules or drug targets are known to perform several roles in the body.

The drugs are designed to interact with specific targets so that these have least chances of affecting the other targets. This minimises the side effects and localises the action of the drug.

Q.3. Name the macromolecules that are chosen as drug targets.

Ans. The macromolecules which are chosen as drug targets are carbohydrates, proteins, lipids and nucleic acids.

Q.4. Why should not the medicines be taken without consulting doctors?

Ans. The drugs or medicines have side effects also. In addition to normal desired therapeutic effect, drugs may also cause other effects which may be beneficial or harmful. These side effects arise because the drug may bind to more than one type of receptor. Therefore, the doctor must be consulted to choose the right drug which has maximum affinity for a particular receptor site to have the desired effect. The doctor will also advise for the correct dose because some drugs like opiates in higher doses may act as poisons leading to serious problems and even may cause death.

Q.5. Define the term chemotherapy. (Hr. S.E. 2011)

Ans. The branch of chemistry which deals with the treatment of diseases using chemicals is called chemotherapy.

Q.6. Which forces are involved in holding the drugs to the active site of enzymes?

Ans. The forces holding drugs to the active sites of enzymes are hydrogen bonding, ionic bonding, dipole-dipole interactions or van der Waals interactions.

Q.7. While antacids and antiallergic drugs interfere with the function of histamines but why do these not interfere with the function of each other?

Ans. Drugs designed to cure some ailments in one organ in the body do not affect the other parts because they work on different receptors. For example, secretion of histamine causes allergy. It also causes acidity due to release of excessive hydrochloric acid in the stomach. Since antiallergic and antacid drugs work on different receptors, therefore, antihistamines cure allergy while antacids remove acidity.

Q.8. Low level of norepinephrine is the cause of depression. What type of drugs are needed to cure this problem? Name two drugs.

Ans. Norepinephrine induces a feeling of well being and helps in changing the mood. If the level of norepinephrine is low, then the signal sending activity of the hormone becomes low and the person suffers from depression. In such cases, the patient needs anti-depressant drugs which inhibit the enzymes which catalyse the degradation of norepinephrine. The common drugs used as anti-depressant are ipronazod and phenelzine.

Q.9. What is meant by the term 'broad spectrum antibiotics'? Explain.

Ans. These are the antibiotics which are effective against several types of harmful micro-organisms. Therefore, these are used to cure a variety of diseases. For example, chloramphenicol is effective against a variety of diseases such as typhoid, acute fever, dysentery, whooping cough, eye infections, certain urine infections, etc. Other broad spectrum antibiotics are tetracycline, ofloxacin, etc.

Q.10. How do antiseptics differ from disinfectants? Give one example of each. (D.S.E. 2011)

Ans. Antiseptics are the chemical substances which are used to either kill or prevent the growth of micro-organisms. These are not harmful to living tissues and can be safely applied on wounds, cuts, diseased skin surfaces. For example, dettol, savlon, furacin, soframycin, etc.

Disinfectants are the chemical substances which kill micro-

organisms but they cannot be applied on living tissues. In other words, they also kill micro-organisms like antiseptics but are not safe for living tissues. These are commonly applied to inanimate objects such as floor, drainage system, instruments, etc. Some common examples of disinfectants are phenol (1% solution), chlorine (0.2 to 0.4 ppm), etc.

Q.11. Why are cimetidine and ranitidine better antacids than sodium bicarbonate or magnesium or aluminium hydroxide?

Ans. If excess of sodium bicarbonate, $Mg(OH)_2$ or $Al(OH)_3$ is used, it will make the stomach alkaline and trigger the production of even more HCl which may cause ulcers in the stomach. In contrast, cimetidine and ranitidine prevent the interaction of histamine with the receptor cells present in the stomach wall. This releases lesser amount of HCl .

Q.12. Name a substance which can be used as an antiseptic as well as disinfectant.

Ans. 0.2% solution of phenol acts as an antiseptic while 1% solution of phenol acts as a disinfectant.

Q.13. What are main constituents of dettol ?

(D.S.B. 2011)

Ans. The main constituent of dettol are chloroxylenol and carphenol in a suitable solvent.

Q.14. What is tincture of iodine ? What is its use ?

(A.I.S.B. 2011)

Ans. 2-5% iodine solution of alcohol-water is called tincture of iodine. It is a powerful antiseptic and is applied on wounds.

Q.15. What are food preservatives ?

Ans. The chemical substances which are added to the food materials to prevent their spoilage and to retain their nutritive value for long periods are called food preservatives. For example, sodium benzoate, sodium metabisulphate, etc.

Q.16. Why is use of aspartame limited to cold foods and drinks ?

Ans. Aspartame is unstable at cooking temperature and decomposes. Therefore, it is used as sugar substitute in cold drinks and soft drinks.

Q.17. What are artificial sweetening agents ? Give two examples.

Ans. The chemical substances which give sweetening effect to food but do not add any calorie to our body are called artificial sweetening agents. For example, saccharin and aspartame.

Q.18. Name the sweetening agent used in the preparation of sweet for a diabetic patient. (D.S.B. 2011)

Ans. Any artificial sweetening agent such as aspartame, saccharin or alitame may be used.

Q.19. What problem arises in using alitame as artificial sweetener ?

Ans. Alitame is a high potency artificial sweetening agent. Therefore, it poses a problem to control the sweetness of the food.

Q.20. How are synthetic detergents better than soaps ?

Ans. The detergents are better than soaps because of the following reasons:

- Detergents can be used for washing even in hard water. On the other hand, soaps cannot be used in hard water.
- Detergents can be used in acidic solutions because they are not readily decomposed in acidic medium. On the other hand, soaps cannot be used in acidic medium because they are decomposed into carboxylic acids in acidic medium.
- Detergents have a stronger cleansing action than soap.

Q.21. Explain the following terms with suitable examples:

- cationic detergents, b) anionic detergents and c) neutral detergents.

Ans. (a) **Cationic detergents** are those which have cationic hydrophobic group. These are mostly acetates, chlorides or bromides of quaternary ammonium salts. For example, cetyltrimethyl ammonium chloride $[\text{CH}_3(\text{CH}_2)_{15}\text{N}^+(\text{CH}_3)_3]$.

(b) **Anionic detergents** are those which have anionic hydrophobic group. These are manufactured from long chain alcohols. For example, sodium lauryl sulphate $[\text{C}_{12}\text{H}_{25}\text{OSO}_3\text{Na}]$.

Sodium *p*-(dodecyl benzene sulphonate)



(c) **Neutral detergents** are esters of high molecular mass with fatty acids. These contain polar groups which can form hydrogen bonds with water. For example, polyethylene glycol stearate $\text{CH}_3(\text{CH}_2)_{16}\text{COO}(\text{CH}_2\text{CH}_2\text{O})_n\text{CH}_2\text{CH}_2\text{OH}$.

Q.22. What are biodegradable and non-biodegradable detergents ? Give one example of each.

Ans. Detergents having straight hydrocarbon chains are easily decomposed by micro-organisms and are called **bio-degradable detergents** e.g., sodium lauryl sulphate, sodium *p*-(dodecyl benzene sulphonate).

The detergents having branched hydrocarbon chains are not easily decomposed by micro-organisms and are called **non-biodegradable detergents** e.g., sodium 4-1,3,5,7-tetramethyloctyl benzene sulphonate.

Q.23. Why do soaps not work in hard water ?

(D.S.B. 2011)

Ans. Hard water contains calcium and magnesium salts. Therefore, in hard water soap gets precipitated as insoluble calcium and magnesium soaps which being insoluble stick to the cloth as gummy mass and blocks the ability of soap to remove oil or grease from the cloth.

Q.24. Can you use soaps and synthetic detergents to check the hardness of water ?

Ans. Soaps give insoluble precipitate of calcium and magnesium soaps in hard water whereas detergents do not give precipitate. Therefore soaps but not detergents can be used to check the hardness of water.

Q.25. Explain the cleansing action of soaps.

Ans. Refer Text Page 25.

Q.26. If water contains dissolved calcium bicarbonate, out of soaps and synthetic detergents which one will you use for cleaning clothes ?

Ans. Calcium bicarbonate makes water hard. Soap will give precipitate with this hard water and therefore, can not be used for cleaning clothes. On the other hand, a synthetic detergent does not give precipitate in hard water because its calcium salt is also soluble in water. Therefore, synthetic detergent can be used for cleaning clothes in hard water.

Q.27. Label the hydrophilic and hydrophobic parts in the following compounds.

(a) $\text{CH}_3(\text{CH}_2)_{15}\text{CH}_2\text{OSO}_3\text{Na}^+$

(b) $\text{CH}_3(\text{CH}_2)_{15}\text{N}^+(\text{CH}_3)_3\text{Br}^-$

(c) $\text{CH}_3(\text{CH}_2)_{16}\text{COO}(\text{CH}_2\text{CH}_2\text{O})_n\text{CH}_2\text{CH}_2\text{OH}$

Ans. (a)	$\text{CH}_3(\text{CH}_2)_{15}$ Hydrophobic part	OSO_3Na Hydrophilic part
(b)	$\text{CH}_3(\text{CH}_2)_{15}$ Hydrophobic part	$\text{N}^+(\text{CH}_3)_3\text{Br}^-$ Hydrophilic part
(c)	$\text{CH}_3(\text{CH}_2)_{16}$ Hydrophobic part	$\text{COO}(\text{CH}_2\text{CH}_2\text{O})_n\text{CH}_2\text{CH}_2\text{OH}$ Hydrophilic part



NCERT

Exemplar Problems

Subjective Questions

NOTE

Objective Questions from Exemplar Problems are given in Competition File page 45

Short Answer Type Questions

1. What is the average molecular mass of drugs?

Ans. About 100 – 600u.

2. Write the uses of medicines.

Ans. Medicines are used in
(i) diagnosis (ii) prevention and
(iii) treatment of diseases

3. What are antiseptics?

Ans. Antiseptics are chemicals which either kill or prevent the growth of microorganisms and are applied to living tissues.

4. Which type of drugs come under antimicrobial drugs?

Ans. (i) Antiseptics, (ii) antibiotics and antimicrobials.

5. Where are receptors located?

Ans. Receptors are embedded in cell membrane

6. What is the harmful effect of hyperacidity?

Ans. Hyperacidity can cause ulcer development in stomach

7. Which site of an enzyme is called allosteric site?

Ans. Sites different from active site of enzyme where a molecule can bind and affect the active site is called allosteric site. Some drugs may also bind at this site.

8. What type of forces are involved in binding of substrate to the active site of enzyme?

Ans. Ionic bonding, dipole-dipole interaction, hydrogen bonding, van der Waals interaction

9. What is the commonality between the antibiotic arsephenamine and azodye?

Ans. Arsephenamine contains $As=As$ linkage which resembles $N=N$ linkages in azodyes.

10. Which class of drugs is used in sleeping pills?

Ans. Tranquilizers

11. Aspirin is pain relieving antipyretic drug but can be used to prevent heart attack. Explain.

Ans. Aspirin prevents platelet coagulation and therefore has antiblood clotting action. Therefore, aspirin can prevent blood clogging in heart.

12. Both antacids and antiallergic drugs are antihistamines but they cannot replace each other. Explain why?

Ans. Both antacids and antiallergic drugs are antihistamines but they cannot replace each other because they work on different receptors.

13. What is a soft soap?

Ans. Soft soaps are potassium salts of fatty acids.

14. If soap has high alkali content it irritates skin. How can the amount of excess alkali be determined? What can be the source of excess alkali?

Ans. Acid-base titration can be used to determine the excess amount of alkali in soap. The excess alkali left after hydrolysis of oil can be the source of alkalinity in soap.

15. Explain why some times foaming is seen in river water near the place where sewage water is poured after treatment?

Ans. Detergents persist in water even after sewage treatment and therefore, cause foaming in river water.

16. Which category of the synthetic detergents is used in toothpaste?

Ans. Anionic detergent

17. Hair shampoos belong to which class of synthetic detergent?

Ans. Cationic detergent

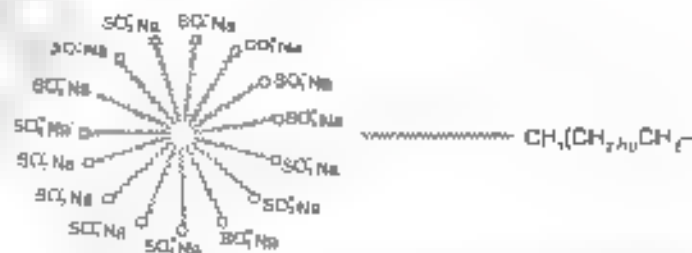
18. Dishwashing soaps are synthetic detergents. What is their chemical nature?

Ans. Non-ionic detergents

19. Draw the diagram showing micelle formation by the following detergent.



Ans.



20. How does the branching of hydrocarbon chain of synthetic detergents affect their biodegradability?

Ans. The detergents having less branching are degraded more easily than branched chain detergents.

21. Why is it safer to use soap from the environmental point of view?

Ans. Soaps are biodegradable. The detergents are quite stable and are non-biodegradable because of branching in hydrocarbon chain hence cause water pollution. Therefore, it is safer to use soap from the environmental point of view.

22. What are analgesics?

Ans. Analgesics are neurologically active pain killing drugs that reduce or abolish pain without causing impairment of consciousness, coordination, mental confusion or paralysis or some other disturbances of nervous system.

23. What is the scientific explanation for the feeling of depression?

Ans. A person suffers from depression when he has low levels of noradrenaline. Noradrenaline is a neurotransmitter which plays a role in mood changes. Low level of noradrenaline lowers the signal-sending activity and make the person suffer from depression.

24. What is the basic difference between antiseptics and disinfectants?

Ans. Antiseptics are applied to living tissues whereas disinfectants are applied to non living objects.

25. Between sodiumhydrogencarbonate and magnesium hydroxide, which is a better antacid and why?

Ans. Magnesium hydroxide is a better antacid because it is insoluble and does not allow the pH to increase above neutral. However, hydrogencarbonate is soluble, and its excessive use can make the stomach alkaline and trigger the production of even more acid.

26. Which analgesics are called opiates?

Ans. Narcotic analgesics which are obtained from opium poppy are called opiates. For example morphine and its derivatives like heroin and codeine.

27. What is the medicinal use of narcotic drugs?

Ans. The narcotic drugs relieve pain and produce sleep. Therefore, these are commonly used for the relief of postoperative pain, cardiac pain and pain of terminal cancer and in child birth.

28. What are antagonist drugs?

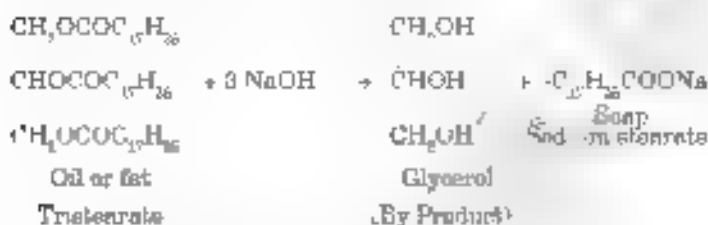
Ans. Drugs which bind to the receptor site and inhibit its natural function are called antagonist drugs.

29. What is the mode of action of antimicrobial drugs?

Ans. Antimicrobial drugs can kill the microorganism such as bacteria, virus, fungi or other parasites. They can inhibit the pathogenic action of microbes.

30. What is the side product of soap industry? Give reactions showing soap formation.

Ans. The side product is glycerol.



31. What is the difference between bathing soap and washing soaps?

Ans. Bathing soaps are potassium salts of long chain fatty acids while washing soaps are sodium salts of long chain fatty acids.

32. How are transparent soaps manufactured?

Ans. Transparent soaps are manufactured by dissolving the soap in ethanol and then evaporating the excess solvent.

33. What is the advantage of using antihistamines over antacids in the treatment of acidity?

Ans. Antacids neutralise the acid produced in the stomach. They do not control the cause of production of excess acid. Therefore, antacids control only the symptoms but not the cause. On the other hand, antihistamines are the drugs which suppress the action of histamine which is the chemical responsible for stimulation of secretion of pepsin and HCl in the stomach. These influence and

prevent the binding of histamine with the receptors present in the stomach wall resulting in lower acid production and therefore, better treatment. This is the advantage of antihistamines over antacids.

34. What are the functions performed by histamine in the body?

Ans. Histamines are the potent vasodilators and perform various functions. For example, histamine contracts the smooth muscles in the bronchi and gut (to which patients of asthma are very sensitive) and relaxes other muscles such as those in the walls of fine blood vessels. Histamine is also responsible for the nasal congestion associated with common colds, coughs, allergic responses to pollens, etc.

35. With the help of an example explain how do tranquilizers control the feeling of depression?

Ans. Noreadrenaline is a tranquilizer which induces the feeling of well being and helps in changing the mood. If the level of noreadrenaline is low due to certain reasons, then the signal sending activity of the hormone becomes low and the person suffers from depression. When antidepressant drugs which inhibit the enzymes are administered, catalyse the degradation of noreadrenaline. If the enzyme is inhibited, the metabolism of important neurotransmitter is slowed down and this can activate the receptor for longer periods of time and therefore, counteract the effect of depression.

36. Why are certain drugs called enzyme inhibitors?

Ans. Enzymes have active sites which bind the substrate for effective and quick chemical reaction. The functional groups present at the active site of enzyme interact with functional groups of substrate through bonding such as ionic bonding, hydrogen bonding, van der Waal interaction etc. Some drugs interfere with this interaction by blocking the binding site of enzyme and prevent the binding of actual substrate with enzyme. This inhibits the catalytic activity of the enzyme. Therefore, these are called inhibitors.

37. What are fillers and what role these fillers play in soap?

Ans. Some substances or fillers are mixed with soaps to affect the properties in order to make it useful for a particular use. For example, sodium rosinate, sodium carboxylate, etc. Sodium rosinate is added in laundry soaps, to increase lather and glycerol is added in shaving soaps, to prevent it from drying.

38. Sugar is the main source of energy as it produces energy on metabolic decomposition. But these days low calorie drinks are more popular, why?

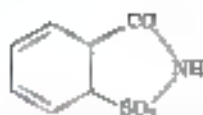
Ans. In low calorie drinks, artificial sweetening agents are present which do not metabolise and hence do not produce energy. For example sucralose. These are called low calorie sweeteners.

39. Pickles have a long shelf life and do not get spoiled for months, why?

Ans. In pickles, plenty of salt and oil are added. These act as preservatives and do not allow bacteria to thrive on them.

40. What is the difference between saccharin and saccharic acid?

Ans. Saccharin is artificial sweetening agent and has the structure



Saccharin

Artificial Sweetener

Saccharic acid is obtained by the oxidation of glucose with conc. HNO_3 .



Saccharic acid
obtained from oxidation of
glucose by conc. HNO_3 .

41. Name an artificial sweetener which is derivative of sucrose.

Ans. Sucralose

42. Name two α -amino acids which form a dipeptide which is 100 times more sweet than cane sugar?

Ans. Aspartic acid and phenylalanine

43. Aspartame is unstable at cooking temperature, where would you suggest aspartame to be used for sweetening?

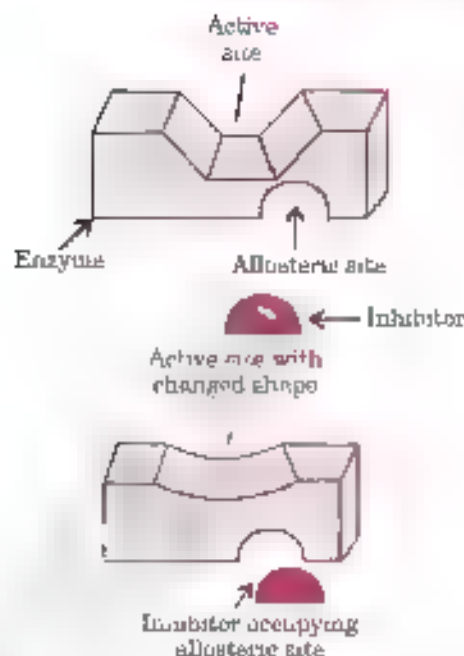
Ans. In cold foods and soft drinks

44. Sodium salts of some acids are very useful as food preservatives. Suggest a few such acids.

Ans. Benzoic acid, sorbic acid, propionic acid

45. Explain the role of allosteric site in enzyme inhibition?

Ans. Some drugs do not bind to the enzyme's active site. These bind to a different site of enzyme which is called allosteric site. This bonding of inhibitor at allosteric site changes the shape of the active site in such a way that the substrate cannot recognise it. As a result, the affinity of the substrate for the active site is reduced.



It may be noted that if the bond formed between enzyme and inhibitor is strong covalent bond and therefore cannot be broken easily then the enzyme gets blocked permanently. The body then degrades the enzyme-inhibitor complex and synthesises new enzyme.

46. How are receptor proteins located in the cell membrane?

Ans. Receptor proteins are embedded in cell membranes in such a way that their small part possessing active sites projects out of the surface of the membrane and opens on the outside region of the cell membrane.

47. What happens when the bond formed between an enzyme and an inhibitor is a strong covalent bond?

Ans. If the bond between an enzyme and an inhibitor is a strong covalent bond and cannot be broken easily, then the enzyme is blocked permanently. The body then degrades the enzyme-inhibitor complex and synthesises the new enzyme.



Quick

MEMORY TEST



A. Say True or False

- Equanil, used as tranquilizer, is a derivative of barbituric acid.
- Phenol acts both as antiseptic and disinfectant.
- Chloroquine is used to cure typhoid.
- Synthetic detergents work well even in hard water.
- In cleansing action of soaps non-polar end is hydrophilic.
- Saccharine and its salts are useful for diabetic patients.
- A 1% solution of phenol is used as an antiseptic.

- Butylated hydroxy anisole is used as artificial sweetening agent.
- Omeprazole and lansoprazole are most effective antacid drugs.
- Mifopristone is used as antifertility drug.

B. Complete the missing links

- Aspartic acts as _____ and _____.
- Ethionoxal is added to soaps to impart them _____ properties.

3. Omeprazole is _____
4. The antiseptic dettol is a mixture of _____ and _____
5. Equanil is a _____
6. Penicillin was discovered by _____
7. The artificial sweetening agent sucralose is a derivative of sucrose
8. _____ are produced when a drug binds to more than one type of receptor
9. The chemical substances which prevent the allergic reactions in body are called _____
10. Chloramphenicol is a _____
11. The birth control pills are called _____ drugs
12. Anil metacresol is _____

G. Choose the correct alternative

1. Arsphenamine is used as *antimicrobial antifertility* drug
2. A 1% solution of phenol acts as *antiseptic / disinfectant*
3. Valium is used as *tranquilizer / antimicrobial*
4. The drug which stimulates or activates the receptor to initiate a physiological response is called *antagonist / agonist*
5. Orneloxolene is *antifertility / antibiotic* drug
6. The inner part or polar part is *hydrophobic / hydrophilic*
7. Soaps are generally *biodegradable / non-biodegradable*
8. BHA is *antimicrobial / antioxidant* in food.
9. Soaps / Synthetic detergents can be used even in hard water
10. Aspartame is *more / less* stable than nitame during cooking.

Answers

Quick

MEMORY TEST



A. Say True or False

1. False 2. True
3. False 4. True
5. False. Nonpolar end behaves as hydrophobic or water repelling part
6. True
7. False. It is used as a disinfectant.
8. False. It is used as antioxidant in food products
9. True. 10. True

B. Complete the missing links

1. antipyretic, analgesic
2. antiseptic 3. antacid

4. chloroxylenol (4-chlorophenol)

5. tranquilizer

7. anefluoro

9. antihistamines

10. broad spectrum antibiotic

11. antifertility

6. Alexander Flemming

8. Side effects

12. antiseptic

C. Choose the correct alternative

1. antimicrobial

3. tranquilizer

5. antifertility

7. biodegradable

9. synthetic detergents

2. disinfectant

4. agonist

6. hydrophilic

8. antioxidant

10. less

HOTS

Higher Order Thinking Skills & Advanced Level

QUESTIONS WITH ANSWERS

Q.1. Amino acids serine, aspartic acid and phenylalanine are present on the active site of an enzyme. Explain which forces may be involved in binding the drug to the enzyme if the drug inhibits the holding of substrate on the active site of enzyme.

Ans. -OH group of serine, -COOH group of aspartic acid and phenyl ring of phenylalanine help to bind the drug to the enzyme

Q.2. Why do drugs designed to cure some ailments in

one organ in the body not affect the other parts? Explain with an example.

Ans. Drugs designed to cure some ailments in one organ in the body do not affect the other parts because they work on different receptors. For example, secretion of histamine causes allergy. It also causes acidity due to release of excessive hydrochloric acid in the stomach. Since antiallergic and antacid drugs work on different receptors, therefore, antihistamines cure allergy while antacids remove acidity.

Q.3. Why are detergents called soapless soaps?

Ans. The synthetic detergents have structures and all the properties similar to soaps but do not contain the usual soaps like sodium salts of fatty acids. Therefore, these are called soapless soaps.

Q.4. How does aspirin help in the prevention of heart attack?

Ans. Most of the heart attacks are due to the clotting of blood in the coronary arteries. Aspirin helps to make the blood thinner and therefore, prevents the formation of blood clots in the coronary arteries. Thus, it prevents heart attacks.

Q.5. Diabetic patients are advised to take artificial sweeteners instead of natural sweeteners. Explain.

Revision Exercises

Very Short Answer Questions (Carrying mark)

- Name one medicine which can act both as analgesic and antipyretic. (H.P.S.B. 2015)
- What type of drug is chloramphenicol? (Pb. S.B. 2009)
- Which substance is generally added to soap to impart antiseptic properties?
- What are broad spectrum drugs? Give one example. (H.P.S.B. 2013, Hr. S.B. 2015, 2018)
- Define antifertility drugs.
- Name the chemical responsible for the antiseptic properties of Dettol.
- Give the structural formula of aspirin. Give the IUPAC name.
- What are anti-oxidants? Give one example. (Hr. S.B. 2017)
- What are antitubercles? Give two examples. (Hr. S.B. 2017, 2018)
- What is the role of bithionol in toilet soaps? (H.P.S.B. 2012)
- Name two artificial sweeteners used in food materials. (H.P.S.B. 2012, Hr. S.B. 2015)
- Name a substance which can be used as an antiseptic as well as disinfectant. (Pb. S.B. 2012, 2013, H.P.S.B. 2012, 2015, 2017)
- What are antimicrobials? Give an example. (J.K.S.B. 2013)
- Give one example of sulphur drugs. (Assam S.B. 2015)
- What is kinetics of iodine and what is it used for? (Pb. S.B. 2013)
- What are antihistamines? Give an example. (J.K.S.B. 2013, Pb. S.B. 2015)
- What are tranquilizers? (H.P.S.B. 2013, Pb. S.B. 2015, Hr. S.B. 2018)

Ans. Diabetic patients do not produce enough insulin to metabolize the natural sugar. As a result, sugar remains in the blood and affects liver, kidneys and heart. Therefore, diabetic patients are advised to take artificial sweeteners such as saccharin. It is not metabolized in the body and is excreted as such from the body without causing any damage to liver, kidneys or heart.

Q.6. Why are detergents non-biodegradable while soaps are biodegradable?

Ans. Common detergents have branched hydrocarbon chains which are either not attacked or attacked only very slowly by bacterium. As a result, the detergents are not degraded in rivers and other waterways and therefore, cause water pollution. On the other hand, soaps have unbranched hydrocarbon chains which are easily degraded by bacteria present in the sewage water and hence do not cause water pollution.

- Name the sweetening agent used in the preparation of sweets for a diabetic patient. (H.P.S.B. 2015)
- Write the main constituents of Dettol. (Hr. S.B. 2015)
- What are antacids? (Pb. S.B. 2015, 2017, Hr. S.B. 2018)
- Define antiseptics and disinfectants. (Hr. S.B. 2017)
- What are food preservatives? (Pb. S.B. 2017)
- What are artificial sweeteners? (Pb. S.B. 2017)
- What are analgesics? (Pb. S.B. 2017)
- What are anti-histamines? Give one example. (Jammu S.B. 2018)
- What is the purpose of adding a food preservative to a packaged food? (West Bengal S.B. 2018)

MCQs from State Boards' Examinations

- Antipyretics are medicinal compounds which
 - lower body temperature
 - relieve pain
 - control malaria
 - kill microorganisms (Meghalaya S.B. 2013)
- 0.2% solution of phenol is an
 - antibiotic
 - antiseptic
 - disinfectant
 - analgesic (Hr. S.B. 2015)
- Which of the following is an analgesic?
 - Ranitidine
 - Aspirin
 - Penicillin
 - None of these (Hr. S.B. 2015)
- Aspirin is an
 - antipyretic
 - antibiotic
 - antiseptic
 - None of these (Jammu S.B. 2018, 2019)
- Acetyl salicylic acid is used as
 - an antiseptic
 - an antibiotic
 - an analgesic
 - a pesticide (Jammu S.B. 2015)

32. Which is used as a preservative to protect processed food?
 a) Sodium sulphate
 b) Saccharin
 c) Sodium bicarbonate
 d) Sodium metabisulphate
33. Dettol is used as
 a) disinfectant (b) antiseptic
 c) analgesic (d) anti-allergic (Hr S.B. 2015)
34. Penicillin is
 a) Hormone (b) Antibiotic
 c) Antiseptic (d) Lipid
 (Jammu S.B. 2016, H P S.B. 2018)
35. Paracetamol is
 a) antiseptic (b) analgesic
 c) antiseptic and analgesic
 d) antibiotic (Jammu S.B. 2016)
36. Which of the following is used as artificial sweetener?
 a) Saccharin (b) Aspirin
 c) Omeprazole (d) Phenaramine (H P S.B. 2018)
37. Which is not a tranquilizer?
 a) Lunatal (b) Seconal
 c) Valium (d) Bithional
 H P S B 2018
38. Which of the following artificial sweeteners is methyl ester of a dipeptide?
 a) Aspartame (b) Sucralose
 c) Saccharin (d) Alitame
 (West Bengal S.B. 2018)
39. Which of the following can be used as an antacid?
 a) Ranitidine (b) Histamine
 c) Equanil (d) Aspirin
 (West Bengal S.B. 2018)
40. The class of drugs used for the treatment of cut or wound is
 a) Tranquillizers (b) Antiseptics
 c) Analgesics (d) Antipyretic
 Pb. S.B. 2018

Short Answer Questions (Carrying 2 or 3 marks)

- Write the structural formula of the following medicinal compounds
 (i) Aspirin
 (ii) Paracetamol
 (iii) Equanil
- What are antibiotics? List two major classes of antibiotics with an example of each class.
- What are broad spectrum antibiotics? Name one such substance.
- What are antifertility drugs? Give two examples.
- Explain why we should not administer aspirin or paracetamol on empty stomach. (Mizoram S.B. 2014)
- Define the following with two examples each.
 a) Antibiotics (b) Antihistamines
 c) Tranquillizers (d) Bithional
 Mizoram S.B. 2014
- What are detergents? Give their scheme of classification. Why are detergents preferred over soaps?
- What are biodegradable and non-biodegradable detergents? What are the consequences of using either class of detergents?
- (a) Why the detergents with straight chain hydrocarbon group are better than the detergents with branched chain hydrocarbon group?
 (b) What type of drug is phenacetin? (Hr S.B. 2006)
- What are antioxidants? What is the difference between preservatives and an antioxidant?
 (Pb.S.B. 2006, 2012, Jammu S.B. 2016)
- Account for the following
 (a) Aspirin drug helps in the prevention of heart attack.
 (b) Diabetic patients are advised to take artificial sweeteners instead of natural sweeteners.
 (c) Detergents are non-biodegradable while soaps are biodegradable. (CBSE Sample Paper 1997)
- Explain the following terms with one suitable example in each case.
 (a) Cationic detergents
 (b) Enzymes
 (c) Antifertility drugs (D.S.B. 2010)
- Explain the following terms with one suitable example for each.
 (i) A sweetening agent for diabetic patients
 (ii) Enzymes
 (iii) Analgesics (D.S.B. 2011)
- What are the following substances? Give one example of each one of them.
 (i) Tranquillizers
 (ii) Food preservatives
 (iii) Synthetic detergents (D.S.B. 2012)
- (a) What is the difference between soaps and detergents?
 (b) What do you mean by food preservatives? Give names of any two food preservatives. (Jharkhand S.B. 2013)
- (a) Sleeping pills are recommended to patient suffering from sleeplessness but it is not advisable to take them without consulting the doctor. Why?
 (b) Why do we require artificial sweetening agents?
 (Assam S.B. 2013)
- (a) Which one of the following is a food preservative?
 Equanil, Morphine, Sodium benzoate
 (b) Why is bithional added to soap?
 (c) Which class of drugs is used in sleeping pills?
 (D.S.B. 2013)
- What are artificial sweetening agents? Write the structural formula of saccharin.
 Or
 Explain the cleansing action of soaps. (Uttarakhand S.B. 2014)
- (a) What are food preservatives? Give an example.
 (b) Mention a drug which can act both as an analgesic as well as an antipyretic. Name an artificial sweetening agent. (Kerala S.B. 2014)

20. a) What is the role of antioxidants in our living systems? Name one famous antioxidant.
b) Give the name of any one neurotransmitter.

Meghalaya S.B. 2014

31. (a) Antibiotics are classified into broad spectrum antibiotics and narrow spectrum antibiotics. Write one example each for these antibiotics.

(b) Write one similarity and one difference between antiseptics and disinfectants. *(Kerala S.B. 2014)*

32. (i) What are disinfectants? Give an example.

(ii) Give two examples of macromolecules that are chosen as drug targets.

(iii) What are anionic detergents? Give an example.

D.S.B. 2014

33. (i) What are antiseptics? Give an example.

(ii) Why is the use of aspartame limited to cold foods and soft drinks? *D.S.B. 2014*

34. (i) Name the sweetening agent used in the preparation of sweets for a diabetic patient.

(ii) What are antihistamines? Give an example.

(D.S.B. 2014)

25. a) Give an example each of the following:

(i) Artificial sweetening agents

(ii) Narcotic analgesics

(b) What are cationic detergents? Give an example.

(Karnataka S.B. 2018)

28. Define antibiotics. How do bactericidal antibiotics differ from bacteriostatic antibiotics? Give one example of each.

Mizoram S.B. 2015

27. a) What are antibiotics? Write the name of first antibiotic discovered.

(b) Give one example of an artificial sweetener used by diabetic patients.

(c) What are antioxidants? *(Meghalaya S.B. 2015)*

28. What are synthetic detergents? Write any four reasons for which they are preferred over soaps.

Mizoram S.B. 2018

Or

What are broad spectrum and narrow spectrum antibiotics? Give one example of each.

(Nagaland S.B. 2018)

39. Give one example each of the following:

i) A non-narcotic analgesic

ii) An artificial sweetener

iii) A food preservative chemical

Or

(a) Mention one advantage of use of synthetic detergent over soap.

(b) What is structure of iodine? Mention one use of it. *Assam S.B. 2016*

30. Explain the cleansing action of soap.

Hr. S.B. 2016, Nagaland S.B. 2018

31. a) Explain with example:

(i) Food preservatives (ii) Detergents

(b) Write the name of a substance that can be used as an antiseptic as well as disinfectant.

Tripura S.B. 2018

32. (a) What is an antiseptic? Give one example.

(b) Name one narcotic and one non-narcotic analgesic.

(c) Name any two main categories of food additives.

Meghalaya S.B. 2018

33. How are antiseptics distinguished from disinfectants? Give one example of each.

Or

(i) What are food additives?

(ii) What are antihistamines?

H.P.S.B. 2016

34. (i) What are tranquilizers?

(ii) What is structure of iodine? Give the constituents of dettol. *H.P.S.B. 2016*

35. (a) What are antagonist and agonist drugs?

(b) Give one example each of bactericidal and bacteriostatic antibiotics. *Assam S.B. 2018*

36. Give one example of each of the following: any three

(i) A tranquiliser

(ii) An antidepressant drug

(iii) Narcotic analgesic

(iv) An antiseptic

Assam S.B. 2017

37. (a) What are antacids? Name two commonly used antacids.

(b) Write difference between antiseptics and disinfectants.

Meghalaya S.B. 2018

38. (i) Name a substance which can act as non-narcotic analgesic.

(ii) What are antibiotics? Give an example of antibiotics.

Or

(i) Why do we require artificial sweetening agents?

(ii) What are antacids? Give one example.

Assam S.B. 2018

39. Antibiotics, antiseptics and disinfectants are antimicrobial drugs. Explain any one of these with examples.

Kerala S.B. 2017

40. (a) Define analgesics.

(b) Define antipyretics.

(c) What is structure of iodine?

H.P.S.B. 2018

41. (a) Why are artificial sweetening agents needed? Give two examples.

Jammu S.B. 2018

(b) Describe briefly the cleansing action of soap.

(Jammu S.B. 2018, Nagaland S.B. 2018)

42. (a) What are drugs?

(b) Write an example for a drug classified based on its chemical structure. *(Kerala S.B. 2018)*

CBSE QUESTIONS

43. Explain the following terms with one example in each case:

(a) Food preservatives

(b) Enzymes

(c) Detergents

(A.I.S.B. 2010)

44. What are analgesic drugs? How are they classified and when are they usually recommended for use?

(A.I.S.B. 2010, D.S.B. 2010)

45. Explain the following terms with an example for each:

(a) Antibiotics

(b) Antiseptics

(c) Analgesics

(A.I.S.B. 2010)

36. Describe the following giving one example for each
 (i) Detergents
 (ii) Food preservatives
 (iii) Antacids (D.S.B. 2011 A.I.S.B. 2011)
47. What is the cause of a feeling of depression in human beings? Name a drug which can be used in treating this depression. (A.I.S.B. 2012)
48. (a) What class of drug is Ranitidine?
 (b) If water contains dissolved Ca^{2+} ions, out of soaps and synthetic detergent, which will you use for cleaning clothes?
 (c) Which of the following is an antiseptic?
 0.2% phenol, 1% phenol (A.I.S.B. 2015)
49. (a) Give an example of artificial sweetener that could have been recommended to diabetic patients.
 (b) What type of analgesics are chiefly used for the relief of pains of terminal cancer? (A.I.S.B. 2014)

50. Define the following:
 (i) Cationic detergents
 (ii) Broad spectrum antibiotics
 (iii) Tranquilizers (D.S.B. 2017 A.I.S.B. 2017)
51. Define the following:
 (i) Anionic detergents
 (ii) Narrow spectrum antibiotics
 (iii) Antacids (D.S.B. 2017 A.I.S.B. 2017)
52. Define the following:
 (i) Anionic detergents
 (ii) Limited spectrum antibiotics
 (iii) Antiseptics (D.S.B. 2017 A.I.S.B. 2017)
53. (a) Why is bithional added to soap?
 (b) What is tincture of iodine? Write its one use.
 (c) Among the following, which one acts as a food preservative?
 Aspartame, Aspirin, Sodium Benzoate, Paracetamol (A.I.S.B. 2018)

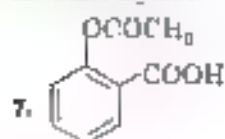


Hints & Answers

for Revision Exercises

Very Short Answer Questions

1. Aspirin 2. Broad spectrum antibiotic
 3. Bithional 4. Chloramphenicol
 5. 4-methylphenol



2-Acetoxybenzoic acid

8. DHT BHA

- (i) It acts as antiseptic

11. Saccharine, aspartame

12. Phenol 14. Sulphadiazine

16. Saccharine 19. Chloroxylenol and terpinol

27. (a) 28. b 29. (b) 30. a 31. c
 32. (d) 33. b 34. b 35. b 36. a
 37. d 38. a 39. a 40. b

Competition File

OBJECTIVE TYPE QUESTIONS

Multiple Choice Questions

M, C, Q.



A TOPICWISE MULTIPLE CHOICE QUESTIONS with only one correct answer

Chemicals in Medicines and Health Care

- A1. Antipyretics are medicinal compounds which
 (a) relieve pain
 (b) lower body temperature

- (c) control malaria
 (d) kill other harmful organisms

A2. Aspirin is

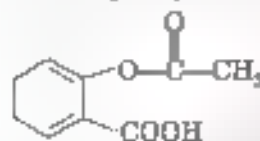
- (a) barbituric acid (b) seconal
 (c) chloroxylenol (d) acetylsalicylic acid

A3. Which of the following is not a tranquilizer?

- (a) Barbituric acid (b) Seconal
 (c) Luminal (d) Phenacetin

Competition File

- A4.** Which of the following is not an antibiotic ?
 a Chloramphenicol (b) Sulphadiazine
 c) Penicillin (d) Bitluonal
- A5.** 2-Acetoxy benzoic acid is
 a antiseptic (b) antipyretic
 c) analgesic (d) mordant dye
- A6.** Which of the following is not an antipyretic ?
 a Paracetamol (b) Aspirin
 c Chloramphenicol (d) Phenacetin
- A7.** Chloramphenicol is
 a antipyretic (b) broad spectrum antibiotic
 c) an dye (d) tranquilizer
- A8.** Aspirin is a
 a narcotic (b) antipyretic
 c) antimalarial (d) antiseptic
- A9.** Sulphonamides act as
 a hypnotics (b) antidepressants
 c) antimicrobials (d) antiseptics
- A10.** Progestogens and oestrogens are used as
 a antacids (b) antifertility drugs
 c) antimicrobials (d) antihistamines
- A11.** Benadryl is used as
 a antiseptic (b) disinfectant
 c) analgesic (d) antihistamine
- A12.** Mifepristone is used as
 a antimicrobial (b) antimalarial
 c) antifertility drug (d) tranquilizer
- A13.** Which of the following can possibly be used as analgesic without causing addiction and modification ?
 a Morphine
 b) N-Acetyl-paraaminophenol
 c) Diazepam
 d) Tetrahydrocannabinol
- A14.** The following compound is used as



- a an anti-inflammatory compound
 b) analgesic
 c) hypnotic
 d) antiseptic
- A15.** Amoxillin is semi-synthetic modification of
 a penicillin (b) streptomycin
 c) tetracycline (d) chloramphenicol

- A16.** A broad spectrum antibiotic is
 (a) paracetamol (b) penicillin
 (c) aspirin (d) chloramphenicol

Chemicals in Food and Cleaning Agents

- A17.** Which of the following is used as an antioxidant in foods ?
 (a) Saccharin (b) Methylated hydroxy anisole
 c) Ormeloxifene (d) Cochineal
- A18.** Which of the following is used as a preservative to protect processed food ?
 (a) Sodium sulphate (b) Saccharin
 (c) Aspartame (d) Sodium metabisulphite
- A19.** Which of the following is artificial sweetening agent ?
 (a) Butylated hydroxy toluene
 (b) Aspartame
 (c) Sodium benzoate
 (d) Terpineol
- A20.** Which of the following is not an artificial sweetening agent?
 (a) Dulcin (b) Aspartame
 (c) Sodium benzoate (d) Aspartame
- A21.** Which of the following is used as an antioxidant in foods?
 a Saccharin (b) Methylated hydroxy anisole
 (c) Ormeloxifene (d) Aspartame
- A22.** Pick the correct statement among the following:
 (a) Sodium dodecylbenzene sulphonate used in tooth paste is a cationic detergent
 b) Sodium lauryl sulphate forms an insoluble scum with hard water
 c) Cetyltrimethyl ammonium bromide is a popular cationic detergent used in hair conditioners
 d) Non-ionic detergents are formed when polyethylene glycol reacts with adipic acid
- A23.** Which among the following detergents is non-ionic in character?
 (a) Sodium lauryl sulphate
 (b) Pentaerythritol stearate
 c) Cetyltrimethyl ammonium chloride
 (d) Sodium n-dodecyl benzene-sulphonate
- A24.** Which of the following is not a food preservative ?
 (a) Sodium chloride (b) Sodium benzoate
 (c) Sodium stearate (d) Sodium metabisulphite
- A25.** Which of the following is not a surfactant ?
 a $\text{CH}_3(\text{CH}_2)_{14}\text{N}^+\text{CH}_3\text{Br}^-$
 b $(\text{CH}_3)_3\text{C}(\text{CH}_2)_{15}\text{NH}_2$
 (c) $\text{CH}_3(\text{CH}_2)_{16}\text{CH}_2\text{OSO}_3\text{Na}^+$
 d $\text{CH}_3(\text{CH}_2)_{16}\text{CH}_2\text{N}^+\text{CH}_3\text{Br}^-$

- A4. a A5. b A6. c A7. b A8. b A9. c A10. b A11. d A12. c A13. b A14. b
 A15. a A16. d A17. b A18. d A19. c A20. c A21. b A22. A23. b A24. c A25. b

Competition File

B (MULTIPLE CHOICE QUESTIONS from competitive examinations

AIPMT & Other State Boards' Medical Entrance

- B1.** Which one of the following is employed as a tranquiliser?
 a. Naproxen b. Tetracycline
 c. Chloropheniramine d. Equanil

(C.B.S.E. PMT 2008)

- B2.** Which one of the following is employed as antihistamine?
 a. Chloramphenicol b. Diphenylhydramine
 c. Norfloxacin d. Omeprazole

A.I.P.M.T. 2011

- B3.** Antiseptics and disinfectants either kill or prevent growth of micro-organisms. Identify which of the following statements is not true.

- (a) Dilute solutions of boric acid and hydrogen peroxide are strong antiseptics.
 (b) Disinfectants harm the living tissues.
 (c) A 0.2% solution of phenol is an antiseptic while 1% solution acts as a disinfectant.
 (d) Chlorine and iodine are used as strong disinfectants.

(NEET 2013)

- B4.** Artificial sweetener which is stable under cold conditions only is

- a. saccharine b. sucralose
 c. aspartame d. alitame

A.I.P.M.T. 2015

- B5.** Ethiconal is generally added to the soaps as an additive to function as a/an

- (a) buffering agent b) Antiseptic
 c) softener d) dryer

A.I.P.M.T. 2015

- B6.** Which of the following is an analgesic?

- a. Streptomycin b. Chloramphenicol
 c. Novargin d. Penicillin

NEET 2010

- B7.** Mixture of chloroxylenol and terpineol acts as

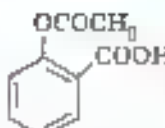
- a. antiseptic b) antipyretic
 c) antibiotic d) analgesic

NEET 2011

- B8.** Tincture of iodine is

- a) aqueous solution of I_2
 b) solution of I_2 in aqueous KI
 c) alcoholic solution of I_2
 d) aqueous solution of KI

A.I.I.M.S. 2000

- B9.** The compound  is used as

- (a) antiseptic b) antibiotic
 (c) analgesic d) pesticides

(A.I.I.M.S. 2007)

- B10.** Which of the following statements is not true?

- (a) Some disinfectants can be used as antiseptic at low concentration.
 (b) Sulphadiazine is a synthetic antibacterial.
 (c) Pheromones provide chemical means of establishing communication.
 (d) Aspirin is analgesic and antipyretic.
 (e) Norfloxacin is a pheromone.

(Kerala PMT 2008)

- B11.** Terfenadine is commonly used as a/an

- (a) tranquilizer b) antihistamine
 (c) antimicrobial d) antibiotic
 (e) antifertility drug

(Kerala PMT 2011)

- B12.** Which one of the following is an antacid

- a) Iproniazid b) Salvarsan
 c) Zalcitabine d) Chloramphenicol
 (e) Terpineol

(Kerala PMT 2012)

- B13.** Drugs that bind to the receptor site and inhibit its natural function are called

- (a) antagonists b) agonists
 (c) enzymes d) molecular targets

A.M.U. Med. 2013

- B14.** The drug Tegamet is

- (a) analgesic b) antidepressant
 (c) anaesthetic d) anesthetic
 (e) antibiotic

Kerala PMT 2015

- B15.** Which one of the following is a cationic detergent?

- (a) Sodium lauryl sulphate
 b) Cetyl trimethylammonium bromide
 c) Sodium dodecylbenzene sulphonate
 d) Glyceryl oleate

Kerala PMT 2015

JEE (Main) & Other State Boards' Engineering Entrance

- B16.** Which one of the following types of drugs reduce fever?

- (a) Antiseptics b) Antipyretics
 (c) Antibiotics d) Tranquilizers

(A.I.E.E.E. 2005)

- B17.** Aspirin is known as

- (a) phenyl salicylate b) acetyl salicylate
 c) methyl salicylic acid d) acetyl salicylic acid

A.I.E.E.E. 2012

- B1. (d) B2. (b) B3. (a) B4. (c) B5. (b) B6. (c) B7. (a) B8. (c) B9. (c) B10. (e)**
B11. (b) B12. (c) B13. (a) B14. (d) B15. (b) B16. (b) B17. (d)

Competition File

- B18.** A drug that is antipyretic as well as analgesic is
 a) chlorpromazine hydrochloride
 b) paracetamol
 c) chloroquin
 d) penicillin (Karnataka C.E.T 2009)
- B19.** Which of the following compounds is not an antacid?
 a) Phenazone, b) Ranitidine
 c) Aluminium hydroxide, d) Cimetidine (JEE Main 2015)
- B20.** Which of the following is an anionic detergent?
 a) Sodium stearate, b) Sodium lauryl sulphate
 c) Cetyltrimethyl ammonium bromide
 d) Glyceryl oleate (JEE Main 2018)
- B21.** Tranquilizers are substances used for the treatment of
 a) cancer, b) AIDS
 c) mental diseases, d) physical disorders
 e) blood infection (Kerala C.E.T 2004)
- B22.** Barbituric acid is used as
 a) an antipyretic, b) an antiseptic
 c) an antibiotic, d) an analgesic
 e) a tranquilizer (Kerala C.E.T 2003)
- B23.** 2-Acetoxy benzoic acid is used as
 a) antismaria, b) antidepressant
 c) antiseptic, d) antipyretic (Karnataka C.E.T 2004)
- B24.** Which of the following is bacteriostatic?
 a) penicillin, b) erythromycin
 c) aminoglycoside, d) ofloxacin
 e) bithional (Kerala C.E.T 2008)
- B25.** Which among the following is not an antibiotic?
 a) Penicillin, b) Oxytocin
 c) Erythromycin, d) Tetracycline
 e) Ofloxacin (Kerala P.E.T 2008)
- B26.** Match the chemicals in column I with their uses in column II
- | Column I | Column II |
|-----------------------|---------------------------|
| A. Sodium perborate | I. Disinfectant |
| B. Chlorine | II. Antiseptic |
| C. Bithional | III. Milk bleaching agent |
| D. Potassium stearate | IV. Soap |
- a) A - I, B - II, C - III, D - IV
 b) A - II, B - III, C - IV, D - I
 c) A - III, B - I, C - II, D - IV
 d) A - IV, B - I, C - II, D - III (D.C.E 2009)
- B27.** Which one among the following is not an analgesic?
 a) Ibuprofen, b) Naproxen
 c) Aspirin, d) Valium (Kerala C.E.T 2009)
- B28.** Which of the following is not an artificial sweetener?
 a) Aspartame, b) Sucralose
 c) Sucrose, d) Allicane (A.M.U. Engg 2010)
- B29.** The class of drugs used for the treatment of stress is
 a) analgesics, b) antiseptics
 c) anxiolytics, d) tranquilizers (J.K.C.E.T 2010)
- B30.** The artificial sweetener containing chlorine that has the appearance and taste as that of sugar and is stable at cooking temperature is
 a) Aspartame, b) Saccharin
 c) Sucralose, d) Allicane (Kerala P.E.T 2010)
- B31.** The cationic detergent that is used in hair conditioners is
 a) sodium dodecylbenzene sulphonate
 b) sodium lauryl sulphate
 c) tetramethyl ammonium chloride
 d) sodium stearyl sulphate
 e) cetyltrimethyl ammonium bromide (Kerala P.E.T 2011)
- B32.** Salts of sorbic acid and propionic acid are used as
 a) antioxidants, b) flavouring agents
 c) food preservatives, d) nutritional supplements
 e) detergents (Kerala P.E.T 2011)
- B33.** The first discovered antibiotic is
 a) streptomycin, b) penicillin
 c) chloramphenicol, d) tetracycline (Odisha J.E.E 2013)
- B34.** Which of the following is antipyretic as well as analgesic?
 a) Sulphaguanidine, b) Paracetamol
 c) Penicillin, d) Phenol (A.M.U. Engg. 2012)
- B35.** Oils are liquids at room temperature since they contain higher percentage of
 a) oleates, b) palmitates
 c) stearates, d) myristates (Karnataka C.E.T 20)
- B36.** Butylated hydroxy toluene as a food additive acts as
 a) antioxidant, b) flavouring agent
 c) colouring agent, d) emulsifier (Karnataka C.E.T 2014)
- B37.** Which among the following detergents is non-ionic in character?
 a) Sodium lauryl sulphate
 b) Pentaerythrityl stearate
 c) Cetyltrimethyl ammonium chloride
 d) Sodium n-dodecyl benzene sulphonate (MH-CET 2015)

B18. b B19. a B20. b) B21. c B22. a B23. d B24. b B25. b B26. c B27. d
 B28. c B29. d B30. c B31. b B32. c B33. b B34. b B35. a B36. a B37. b

Competition File

B38. Which among the following is a tranquilizer?

- (a) Aspirin (b) Valium
(c) Penicillin (d) Sulphadiazide

MH-CET 2015

B39. Which of the following is an analgesic?

- (a) Ofloxacin (b) Penicillin
(c) Aminoglycosides (d) Paracetamol

MH-CET 2016

B40. What is the combining ratio of glycerol and fatty acids when they combine to form triglyceride?

- (a) 3 : 4 (b) 3 : 2
(c) 1 : 3 (d) 1 : 2

MH-CET 2016

B41. Narcotic analgesics are

- (a) aspirin (b) paracetamol
(c) codeine (d) zantac
(e) cimetidine

Kerala PET 2016

B42. Which of the following is employed as tranquilizer?

- (a) Equanil (b) Naproxen
(c) Tetracycline (d) Dettol

(Kerala PET 2016)

B43. Bactericidal antibiotic among the following is

- (a) ofloxacin (b) erythromycin
(c) chloramphenicol (d) tetracycline

Karnataka CET 2017

B44. Pick the correct statement among the following

- (a) Sodium dodecylbenzene sulphate used in tooth paste is a cationic detergent
(b) Sodium lauryl sulphate forms an insoluble scum with hard water
(c) Cetyltrimethyl ammonium bromide is a popular cationic detergent used in hair conditioner
(d) Non-ionic detergents are formed when polyethylene glycol reacts with adipic acid

Karnataka CET 2017

B45. Phenol is highly corrosive substance. Its 0.2 percent solution is used as

- (a) antibiotic (b) antiseptic
(c) disinfectant (d) antihistamine
(e) analgesic

Kerala PET 2017

B46. Some drugs are potent

- (a) hypnotics (b) antimicrobials
(c) antacids (d) antiseptics
(e) antiallergics

(Kerala PET 2018)

B38. (b) B39. (d) B40. (c) B41. (c) B42. (a) B43. (a) B44. (c) B45. (b) B46. (a)

C (MULTIPLE CHOICE QUESTIONS with more than one correct answer

C1. The chemicals used as analgesics are

- (a) naproxen (b) sulphadiazine
(c) dicyclanole sodium (d) serotonin

C2. Which of the following are not used as antacids?

- (a) Magnesium trisilicate (b) Sodium bicarbonate
(c) Magnesium sulphate (d) Bismuth

C3. Which of the following is/are used as antioxidants for food stuffs?

- (a) BHA (b) Sodium stearate
(c) Ascorbic acid (d) Sodium sulphate

C4. Which of the following is/are used as artificial sweeteners?

- (a) Saccharin (b) Aspartame
(c) Omeprazole (d) Phenacetin

C5. Which of the following act as antihistamines?

- (a) Dimethidene (b) Phenacetin
(c) Diphenhydramine (d) Luminal

C6. Which of the following is/are not derivative of barbituric acid used as tranquilizer?

- (a) Equanil (b) Serotonin
(c) Secobarbital (d) Luminal

C7. Which of the following is/are not antiseptic?

- (a) Bithional (b) Hydrogen peroxide
(c) Petidine (d) Dicyclanole sodium

C8. Which of the following are synthetic detergents?

- (a) $\text{CH}_3(\text{CH}_2)_{15}\text{COOCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OH}$
(b) $\text{CH}_3(\text{CH}_2)_{15}\text{COONa}$
(c) $\text{CH}_3(\text{CH}_2)_{15}\text{N}(\text{CH}_3)^+\text{Cl}^-$
(d) $(\text{CH}_3(\text{CH}_2)_{15}\text{COO})_2\text{Mg}$

C1. (a, c) C2. (c, d) C3. (a, d) C4. (a, b) C5. (a, b, c) C6. (a, b) C7. (c, d)
C8. (a, c)

Assertion Reason Type Questions

The questions given below consist of an Assertion and the Reason. Use the following key to choose the appropriate answer

- (a) If both assertion and reason are CORRECT and reason is the correct explanation of the assertion.

- (b) If both assertion and reason are CORRECT but reason is NOT THE CORRECT explanation of the assertion.
(c) If assertion is CORRECT but reason is INCORRECT
(d) If assertion is INCORRECT but reason is CORRECT
(e) If both assertion and reason are INCORRECT

Competition File

- 1. Assertion :** Detergents are preferred to soaps for washing purposes.
Reason : Detergents having branched chain hydrocarbon are non-biodegradable.
- 2. Assertion :** Aspirin can cause ulcer in stomach when taken empty stomach.
Reason : Aspirin gets hydrolysed to acetylic acid in stomach where pH is 2.
- 3. Assertion :** Combinations of progesterone and estrogen are used as antifertility drugs.
Reason : These control the pregnancy.
- 4. Assertion :** Certain narcotics are used as analgesics.
Reason : Narcotics lower the body temperature in high fever.
- 5. Assertion :** Penicillin has a narrow spectrum.
- Reason :** Acid gastritis is common ailment associated with digestion.
- 6. Assertion :** Pheniramine is used as an antihistaminic.
Reason : Antacid/analgesics are used for treatment of gastric ulcers.
- 7. Assertion :** A 0.2% solution of phenol is an antiseptic while 1% solution is a disinfectant.
Reason : Disinfectant = kill microorganisms but are harmful to human tissues.
- 8. Assertion :** Sodium-2-sulphate benzene sulphamate is a biodegradable detergent.
Reason : Detergents having highly branched chains are biodegradable. A I I M S, 2009
- 9. Assertion :** Saccharin is an artificial sweetener.
Reason : It has a high caloric value.
- 10. Assertion :** Aspartame is used as artificial sweetener in cold drinks.
Reason : Aspartame is stable under cold conditions.

1. (b) 2. (a) 3. (a) 4. (c) 5. (b) 6. (a) 7. (b) 8. (c) 9. (c) 10. (a)

Matrix Match Type Questions

Each question contains statements given in two columns, which have to be matched. Statements in Column I are labelled as A, B, C and D whereas statements in Column II are labelled as p, q, r and s. Match the entries of Column I with appropriate entries of Column II. Each entry in Column I may have one or more than one correct option from Column II. The answers to these questions have to be appropriately bubbled as illustrated in the following example.

If the correct matches are A-q, A-r, B-p, B-s, C-r, C-s and D-q, then the correctly bubbled matrix will look like the following.

	p	q	r	s
A	<input checked="" type="radio"/>	<input checked="" type="radio"/>	<input type="radio"/>	<input type="radio"/>
B	<input type="radio"/>	<input checked="" type="radio"/>	<input type="radio"/>	<input checked="" type="radio"/>
C	<input type="radio"/>	<input type="radio"/>	<input checked="" type="radio"/>	<input checked="" type="radio"/>
D	<input type="radio"/>	<input checked="" type="radio"/>	<input type="radio"/>	<input type="radio"/>

1. Match the drug in Column I with its type given in Column II.

Column I	Column II
A) Floxacin	p. Antiseptic
B. Phenol	q. Bactericidal
C) Tetracycline	r) Antibiotic
D. Dettol	s. Disinfectant

(1) (A) q), (r) (B) (p), (s) (C) (r) (D) s

Integer Type Questions

Integer Type : The answer to each of the following question is a single-digit-integer ranging from 0 to 9.

1. The number of non-narcotic analgesics among the following are
 aspirin, ibuprofen, morphine, heroin, diclofenac sodium, paracetamol, codeine, naproxen, ipromazid

2. How many of the following are food preservatives?
 potassium metabisulphite, aspartame, sodium benzoate, BHA, saccharin, ahtame, dulcin
3. The number of artificial food sweeteners among the following is
 ahtame, butylated hydroxytoluene, sucralose, terbufundine, dulcin, cinehdine, saccharin, aspartame, sulphadiazine
4. The number of antibiotics among the following is
 ampicillin, sulphadiazine, veronal, squanid, serotomun, amoxil, secoral

ANSWERS

1. 6 2. 3 3. 5 4. 1

Competition File



NCERT

Exemplar Problems
Objective Questions

1. Which of the following statements is not correct?

- (a) Some antiseptics can be added to soaps
(b) Dilute solutions of some disinfectants can be used as antiseptic
(c) Disinfectants are antimicrobial drugs.
(d) Antiseptic medicines can be ingested

2. Which is the correct statement about birth control pills?

- (a) Contain oestrogen only
(b) Contain progesterone only
(c) Contain a mixture of oestrogen and progesterone derivatives
(d) Progesterone enhances ovulation.

3. Which statement about aspirin is not true

- (a) Aspirin belongs to narcotic analgesics
(b) It is effective in relieving pain
(c) It has antillood clotting action.
(d) It is a neurologically active drug.

4. The most useful classification of drugs for medicinal chemists is

- (a) on the basis of chemical structure
(b) on the basis of drug action
(c) on the basis of molecular targets
(d) on the basis of pharmacological effect

5. Which of the following statements is correct?

- (a) Some tranquilisers function by inhibiting the enzymes which catalyse the degradation of noreadrenaline.
(b) Tranquilisers are narcotic drugs
(c) Tranquilisers are chemical compounds that do not affect the message transfer from nerve to receptor
(d) Tranquilisers are chemical compounds that can relieve pain and fever

6. Salvarsan is arsenic containing drug which was first used for the treatment of

- (a) syphilis (b) typhoid
(c) meningitis (d) dysentery

7. A narrow spectrum antibiotic is active against

- (a) gram positive or gram negative bacteria
(b) gram negative bacteria only
(c) single organism or one disease.
(d) both gram positive and gram negative bacteria

8. The compound that causes general antidepressant action on the central nervous system belongs to the class of

- (a) analgesics (b) tranquilizers
(c) narcotic analgesics (d) antihistamines

9. Compound which is added to soap to impart antiseptic properties is

- a. sodium laurylsulphate
b. sodium dodecylbenzenesulphonate
c. rocam
d. bithional

10. Equanil is

- a. artificial sweetener (b) tranquilizer
c. antihistamine (d) antifertility drug

11. Which of the following enhances leathering property of soap?

- a. Sodium carbonate (b) Sodium rosinate
c. Sodium stearate (d) Trisodium phosphate

12. Glycerol is added to soap. It functions

- a. as a filler
b. to increase leathering
c. to prevent rapid drying
d. to make soap granules

13. Which of the following is an example of liquid dishwashing detergent?

- a. $\text{CH}_3(\text{CH}_2)_{16}\text{CH}_2\text{OSO}_3\text{Na}^+$

- b. $\text{C}_6\text{H}_{13}\text{O}-\text{C}_6\text{H}_4-\text{O}-(\text{CH}_2-\text{CH}_2-\text{O})_8-\text{CH}_2\text{CH}_2\text{OH}$

- c. $\text{CH}_3-\text{C}_6\text{H}_4-\text{SO}_3\text{Na}^+$

- d. $\left[\begin{array}{c} \text{CH}_3 \\ | \\ \text{CH}_3(\text{CH}_2)_{15}-\text{N}-\text{CH} \\ | \\ \text{CH}_3 \end{array} \right]^+ \text{Br}^-$

14. Polyethyleneglycols are used in the preparation of which type of detergents?

- a. Cationic detergents (b) Anionic detergents
c. Non-ionic detergents (d) Soaps

15. Which of the following is not a target molecule for drug function in body?

- a. Carbohydrates (b) Lipids
c. Vitamins (d) Proteins

16. Which of the following statements is not true about enzyme inhibitors?

- a. Inhibit the catalytic activity of the enzyme
b. Prevent the binding of substrate
c. Generally a strong covalent bond is formed between an inhibitor and an enzyme
d. Inhibitors can be competitive or non-competitive

Answers

1. (d) 2. c 3. a 4. (a) 5. a 6. a 7. (a) 8. b 9. (d) 10. (b)
11. b 12. c 13. (b) 14. (c) 15. (c) 16. c

Competition File

17. Which of the following chemicals can be added for sweetening of food items at cooking temperature and does not provide calories?

- a. Sucrose (b) Glucose
c. Aspartame (d) Sucralose

18. Which of the following will not enhance nutritional value of food?

- a. Minerals (b) Artificial sweeteners
c. Vitamins (d) Amino acids

▶▶ Matching Type Questions (Type I) ◀◀

Note : In the following questions two or more options may be correct.

19. Which of the following statements are **incorrect** about receptor proteins?

- a. Majority of receptor proteins are embedded in the cell membranes.
b. The active site of receptor proteins opens on the inside region of the cell.
c. Chemical messengers are received at the binding sites of receptor proteins.
d. Shape of receptor doesn't change during attachment of messenger.

20. Which of the following are not used as food preservatives?

- a. Table salt (b) Sodiumhydrogencarbonate
c. Cane sugar (d) Benzoic acid

21. Compounds with antiseptic properties are

- a. CH_3I
b. CH_3Cl
c. Boric acid
d. 0.5 ppm aqueous solution of Cl_2

22. Which of the following statements are correct about barbiturates?

- a. Hypnotics or sleep producing agents
b. These are tranquilizers
c. Non-narcotic analgesics
d. Pain reducing without disturbing the nervous system

23. Which of the following are sulphur drugs?

- a. Sulphapyridine (b) Penicillin
c. Salvarsan (d) Nardal

24. Which of the following are antidepressants?

- a. Imipramine (b) Phenelzine
c. Equanil (d) Salvarsan

25. Which of the following statements are incorrect about penicillin?

- a. An antibacterial fungus
b. Ampicillin is its synthetic modification
c. It has bacteriostatic effect
d. It is a broad spectrum antibiotic

26. Which of the following compounds are considered as antacids?

- a. Sodium carbonate
b. Sodium hydrogencarbonate
c. Aluminium carbonate
d. Magnesium hydroxide

27. Amongst the following antihistamines, which are antacids?

- a. Ranitidine (b) Brompheniramine
c. Terfenadine (d) Cimetidine

28. Veronal and nembutal are derivatives of barbituric acid which are

- a. Tranquilizers (b) Non-narcotic analgesic
c. Antiallergic drugs (d) Neurologically active drugs

29. Which of the following are anionic detergents?

- a. Sodium salts of sulphonated long chain alcohol.
b. Ester of stearic acid and polyethylene glycol
c. Quaternary ammonium salt of amine with acetate ion.
d. Sodium salts of sulphonated long chain hydrocarbons

30. Which of the following statements are correct?

- a. Cationic detergents have germicidal properties
b. Bacteria can degrade the detergents containing highly branched chains
c. Some synthetic detergents can give foam even in ice cold water
d. Synthetic detergents are not soaps

▶▶ Matching Type Questions ◀◀

Note : Match the items given in Column I with the items given in Column II

31. Match the medicines given in Column I with their use given in Column II

Column I	Column II
a. Ranitidine	— Tranquilizer
b. Fentanyl	— Antacid
c. Phenelzine	— Antihistamine
d. Chloramphenicol	a. Antiseptic
	b. Antifertility drug

32. Match the soaps given in Column I with items given in Column II

Column I	Column II
a. Soap chips	dried miniature soap bubbles
b. Soap granules	small broken pieces of soap formed from melted soaps
c. Soap powder	i. soap powder + abrasives + builders like Na_2CO_3 , Na_3PO_4
d. Scouring soap	ii. soap powder + builders like Na_2CO_3 and Na_3PO_4

17. (d) 18. b 19. (b), (c) 20. a, c 21. (b), (c) 22. a, b 23. a, b 24. a, b, c

25. (b), (d) 26. (b), (d) 27. (a), (d) 28. (a), (d) 29. (a), (d) 30. (a), (c), (d)

31. a — ii, b — i, c — ii, d — i 32. a — ii, b — ii, c — i, d — i

Competition File

33. Match structures given in Column I with the type of detergents given in Column II

Column I	Column II
(a) $\text{CH}_3(\text{CH}_2)_{18}\text{COO}(\text{CH}_2\text{CH}_2\text{O})_6\text{CH}_2\text{CH}_2\text{OH}$	(i) Cationic detergent
(b) $\text{C}_{17}\text{H}_{35}\text{COO}^-\text{Na}^+$	(ii) Anionic detergent
(c) $\text{CH}_3-(\text{CH}_2)_{12}\text{CH}_2\text{SO}_3^-\text{Na}^+$	(iii) Non-ionic detergent
(d) $\left[\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_2(\text{CH}_2)_{15}-\text{N}^+-\text{CH}_3 \\ \\ \text{CH}_3 \end{array} \right] \text{Br}^-$	(iv) Soap

34. Match the detergents given in Column I with their uses given in Column II.

Column I	Column II
(a) $\left[\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_2(\text{CH}_2)_{17}-\text{N}^+-\text{CH}_3 \\ \\ \text{CH}_3 \end{array} \right] \text{Br}^-$	(i) Dishwashing powder
(b) $\text{CH}_3-(\text{CH}_2)_{14}-\text{C}_6\text{H}_4-\text{SO}_3^-\text{Na}^+$	(ii) Laundry soap
(c) $\text{C}_{15}\text{H}_{31}\text{COONa} + \text{Na}_2\text{CO}_3 + \text{Rosin}$	(iii) Hair conditioners
(d) $\text{H}_2\text{C}(\text{CH}_2)_{16}\text{CH}_2\text{OH} + \text{H}_2\text{N}(\text{CH}_2)_6\text{NH}_2 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{N}(\text{CH}_2)_6\text{NH}_2$	(iv) Toothpaste

35. Match the class of compounds given in Column I with their functions given in Column II

Column I	Column II
(a) Antagonists	Transmit message between two neurons and that between neurons to muscles
(b) Agonists	(i) Bind to the receptor site and inhibit its natural function
(c) Chemical messenger	(ii) Crucial to body's communication process
(d) Inhibitors	(iii) Mimic the natural messenger
(e) Receptors	(iv) Inhibit activities of enzymes

36. Match the classes of drugs given in Column I with their action given in Column II

Column I	Column II
(a) Analgesics	Inhibit the growth of microorganisms; can be given orally
(b) Antiseptics	(i) Treatment of stress
(c) Antihistamines	(ii) Applied to inanimate objects
(d) Antacids	(iii) Prevents the interaction of histamine with its receptor
(e) Tranquillizers	(iv) Pain killing effect
(f) Antibiotics	(v) Applied to diseased skin surfaces
(g) Disinfectants	(vi) Treatment of acidity

33. (a) (iii), (b) (ii), (c) (i), (d) (iv)

34. (a) (ii), (b) (iv), (c) (i), (d) (iii)

35. (a) (ii), (b) (iv), (c) (i), (d) (iii), (e) (i)

36. (a) (iv), (b) (ii), (c) (vi), (d) (iii), (e) (v), (f) (i), (g) (vi)

Competition File

▶▶▶ Assertion and Reason (Competitive) ▶▶▶

Note: In the following questions a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices.

- (a) Assertion and reason both are correct statements but reason does not explain assertion
 (b) Assertion and reason both are correct and reason explains the assertion
 (c) Both assertion and reason are wrong statements.
 (d) Assertion is correct statement, reason is wrong statement
 (e) Assertion is wrong statement, reason is correct statement
37. **Assertion:** Penicillin G is an antihistamine.
Reason: Penicillin G is effective against gram positive as well as gram negative bacteria.
38. **Assertion:** Sulpha drug contain sulphonamide group.
Reason: Salvarsan is a sulpha drug.
39. **Assertion:** Receptors are crucial to body's communication process.
Reason: Receptors are proteins.
40. **Assertion:** Enzymes have active sites that hold substrate molecule for a chemical reaction.
Reason: Drugs compete with natural substrate by attaching covalently to the active site of enzyme.
41. **Assertion:** Chemical messengers are chemicals that enable communication of message between two neurones or between neurones and muscles.
Reason: Chemicals enter the cell through receptor.
42. **Assertion:** Transparent soaps are made by dissolving soaps in ethanol.

Reason: Ethanol makes things invisible.

43. **Assertion:** Sodium chloride is added to precipitate soap after saponification.
Reason: Hydrolysis of esters of long chain fatty acids by alkali produces soap in colloidal form.
44. **Assertion:** Competitive inhibitors compete with natural substrate for their attachment on the active sites of enzymes.
Reason: In competitive inhibition, inhibitor binds to the allosteric site of the enzyme.
45. **Assertion:** Non-competitive inhibitor inhibits the catalytic activity of enzyme by binding with its active site.
Reason: Non-competitive inhibitor changes the shape of the active site in such a way that substrate can't recognise it.
46. **Assertion:** Chemical messenger gives message to the cell without entering the cell.
Reason: Chemical messenger is received at the binding site of receptor proteins.
47. **Assertion:** Receptor proteins show selectivity for one chemical messenger over the other.
Reason: Chemical messenger binds to the receptor site and inhibits its natural function.
48. **Assertion:** All chemicals added to food items are called food preservatives.
Reason: All these chemicals increase the nutritive value of the food.
49. **Assertion:** Preservatives are added to food items.
Reason: Preservatives inhibit the growth of microorganisms.
50. **Assertion:** Artificial sweeteners are added to the food to control the intake of calories.
Reason: Most of the artificial sweeteners are inert and do not metabolise in the body.

- | | | | | | | | | |
|---------|---------|---------|---------|---------|---------|---------|---------|---------|
| 37. (c) | 38. (d) | 39. (a) | 40. (d) | 41. (d) | 42. (d) | 43. (b) | 44. (d) | 45. (c) |
| 46. (b) | 47. (d) | 48. (c) | 49. (b) | 50. (b) | | | | |

Hints & Explanations for Difficult Objective Type Questions

B. mcq from Competitive Examinations

- B7. **a:** Dettol is a mixture of chloroxylenol and terpineol and acts as antiseptic.
- B8. **a:** Floxacin is bactericidal antibiotic.
- B44. **c:** Cetyltrimethyl ammonium bromide is cationic detergent and has excellent germicidal properties and are used in hair conditioners.
- B. **a:** Aspirin is a non-narcotic analgesic.
18. **b:** Non-ionic detergents are used as liquid dish washing detergents.
19. **c:** Generally a weak bond such as hydrogen bonding, van der Waals interactions is formed between the enzyme and the inhibitor.

JOO

NCERT Exemplar Problems MCQs Type-I

1. **d:** Antiseptics cannot be ingested.

Unit Practice Test

for Board Examination

(Polymers & Chemistry In Everyday Life)

Time allowed : 2 Hrs.

Maximum Marks : 35

1. Is $4\text{NH}-\text{CHR}-\text{CO}_2$ a homopolymer or a copolymer? (1)
2. Write the names and structures of monomers of buna-3. (1)
3. Give one example of a neutral detergent. (1)
4. Name a substance which can be used as disinfectant as well as antiseptic. 1
5. Why is bithional added to soap? (1)
6. What is meant by the term 'broad spectrum antibiotics'? Explain. 2
7. What are biodegradable polymers? Give two examples. (2)
8. What is vulcanization of rubber? Discuss the main purpose of vulcanization of rubber. 2
9. State the function with one example each of
 - i) antihistamines
 - ii) analgesics
 (2)
10. Why are detergents non-biodegradable while soaps are biodegradable? (2)
11. Write the monomers with structures of the following polymers
 - (i) Nylon 6, 6
 - ii) Bakelite
 - iii) Teflon
 (3)
12. Explain the following with examples
 - i) Elastomers
 - ii) Biodegradable polymers
 - iii) Step growth polymerisation.
 (3)
13. Explain the following with example
 - i) Antacids
 - ii) Artificial sweetening agents
 - iii) Antifertility drugs.
 (3)
14. a) Why do drugs designed to cure ailments in one organ in the body not affect the other part? Explain with an example. 3
 b) Low level of noradrenaline is the cause of depression. What types of drugs are needed to cure this problem? 3
15. Discuss the mechanism of free radical cationic polymerisation. (3)
16. (a) How will you distinguish between
 - (i) addition and condensation polymerisation
 - ii) thermoplastic and thermosetting polymers.
 b) What are artificial sweetening agents? Give two examples.
 c) Explain the cleansing action of soaps or detergents. (5)

► To check your performance see HINTS AND SOLUTIONS TO SOME QUESTIONS at the end of Part II of the book

General Instructions

- All questions are compulsory.
- Question numbers 1–8 are very short answer type questions carrying 1 mark each.
- Question numbers 9–14 are short answer type questions carrying 2 marks each.
- Question numbers 15–24 are also short answer type questions carrying 3 marks each.
- Question numbers 25–27 are long answer type questions carrying 5 marks each.

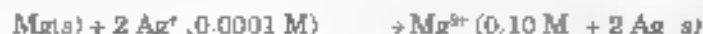
1. Which of the following is more stable complex and why?
 $[\text{Co}(\text{en})_3]^{3+}$ or $[\text{Co}(\text{NH}_3)_6]^{3+}$ (1)
2. Why are carbohydrates generally optically active? (1)
3. Give an example of an artificial sweetener used by diabetic patients. (1)
4. Write the structure of 4-methylpent-3-en-2-one. (1)
5. In the ring test identification of nitrate ion, what is the formula of the compound responsible for the brown ring formed at the interface of two liquids? (1)
6. Draw the structures of the following molecules:
 - (i) XeOF_4
 - (ii) BrF_3 (2)
7. Write the chemical equations for all the steps involved in the rusting of iron. Give any one method to prevent rusting of iron. (2)
8. A colloidal solution of AgI is prepared by the following two methods:
 - (a) Adding AgNO_3 to KI (aq) solution.
 - (b) Adding KI to AgNO_3 (aq) solution.
 - (i) What is the charge of colloidal particles in (a) and (b)?
 - (ii) Give reasons for the origin of charges. (2)
9. Complete the reactions:
 - (i) $\text{Mg}_3\text{N}_2 + \text{H}_2\text{O} \rightarrow$
 - (ii) $\text{POCl}_3 + \text{H}_2\text{O} \rightarrow$ (2)

Or

When conc. H_2SO_4 was added into an unknown salt present in a test tube, a brown gas A was evolved. This gas intensified when copper turnings were also added into the test-tube. On cooling, the gas A changed into a colourless gas B.

 - (a) Identify the gases A and B.
 - (b) Write the equations for the reactions involved.
10. Complete and name the following reactions:
 - (a) $\text{RNH}_2 + \text{CHCl}_3 + \text{KOH} \rightarrow$
 - (b) $\text{RCONH}_2 + \text{Br}_2 + \text{NaOH} \rightarrow$ (2)
11. Define the following:
 - (i) Fuel cell.
 - (ii) Limiting molar conductivity. (2)
12. How are the following conversions carried out?
 - (i) Ethyl chloride to propanoic acid
 - (ii) 2-chloropropane to propan-1-ol. (2)

13. (a) Why is pheno. more acidic than ethanol?
 (b) Give chemical test to distinguish between the following
 (i) 1-Propanol and 2-propanol (ii) Phenol and cyclohexanol (3)
14. (a) Give plausible explanation for each of the following
 (i) Why are primary amines higher boiling than tertiary amines?
 (ii) Why are aliphatic amines stronger bases than aromatic amines? (3)
 (b) How will you convert *p*-toluidine into 2-bromo-4-methylaniline?
15. The following chemical reaction is occurring in an electrochemical cell.



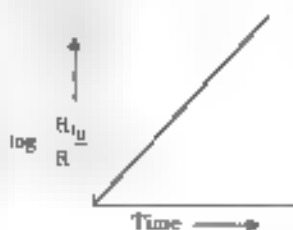
The E° electrode values are

$$\text{Mg}^+/\text{Mg} = -2.36 \text{ V}$$

$$\text{Ag}^+/\text{Ag} = 0.81 \text{ V}$$

For this cell, calculate/write

- (a) (i) E° value for the electrode $2\text{Ag}^+/2\text{Ag}$
 (ii) Standard cell potential E°_{cell}
 (b) Cell potential E_{cell}
 (c) (i) Symbolic representation of the above cell.
 (ii) Will the above cell reaction be spontaneous? (3)
16. Account for the following facts
 (a) The reduction of a metal oxide is easier if the metal formed is in liquid state at the temperature of reduction
 (b) The reduction of Cr_2O_3 with Al is thermodynamically feasible, yet it does not occur at room temperature.
 (c) Pine oil is used in froth flotation method, (3)
17. (a)



Answer the following questions on the basis of the above curve for a first order reaction, $A \rightarrow P$

- (i) What is the relation between slope of this line and rate constant?
 (ii) Calculate the rate constant of the above reaction if the slope is $2 \times 10^{-3} \text{ s}^{-1}$
 (b) Derive the relationship between half-life of a first order reaction and rate constant (3)
18. Explain the following
 (i) H_3PO_2 and H_3PO_3 act as good reducing agent while H_3PO_4 does not
 (ii) All the five bonds in PCl_5 are not equivalent
 (iii) Sulphur in vapour phase is paramagnetic. (3)
19. (a) The decomposition of $\text{N}_2\text{O}_5(\text{g})$ is a first order reaction with a rate constant of $6 \times 10^{-3} \text{ sec}^{-1}$ at 45°C .



If initial concentration of N_2O_5 is 0.25 M , calculate its concentration after 2 min. Also calculate half-life for decomposition of $\text{N}_2\text{O}_5(\text{g})$

(b) For an elementary reaction $2A + B \rightarrow 3C$

the rate of appearance of C at time 't' is $1.3 \times 10^{-4} \text{ mol l}^{-1} \text{ s}^{-1}$

Calculate at this time

(i) rate of the reaction, (ii) rate of disappearance of A

(3)

20. (a) Give the number of unpaired electrons in the following complex ions on the basis of crystal field theory

$[\text{FeF}_6]^{4-}$ and $[\text{Fe}(\text{CN})_6]^{4-}$

(b) Name the isomerism exhibited by the following pair of coordination compounds

$[\text{Co}(\text{NH}_3)_5 \text{Br}] \text{SO}_4$ and $[\text{Co}(\text{NH}_3)_4 \text{SO}_4] \text{Br}$

(2)

Give one chemical test to distinguish between these two compounds.

(c) Draw geometrical and optical isomers of $[\text{CoCl}_2(\text{en})_2]^+$

21. (a) Which will have a higher boiling point?

1-Chloro ethane or 2-methyl 2-chlorobutane

Give reasons

(b) p-nitrochlorobenzene undergoes nucleophilic substitution faster than chlorobenzene. Explain giving the resonating structures as well.

(3)

22. Despite having an aldehyde group

(a) Glucose does not give 2,4-DNP test. What does this indicate?

(b) Draw the Haworth structure of α -D- (+)-glucopyranose

(c) Give the reaction of glucose with nitric acid.

(2)

An optically active amino acid A, can exist in three forms depending on the pH of the medium. If the molecular formula of (A) is $\text{C}_6\text{H}_7\text{NO}_3$, write

(i) Structure of compound A in aqueous medium. What are such ions called?

(ii) In which medium will the cationic form of compound (A) exist?

(iii) In alkaline medium, towards which electrode will the compound A migrate in electric field?

23. (a) What are thermosetting and thermoplastics? Give one example in each case

(b) Give the monomers of Buna-S.

(2)

24. What are the following substances? Give one example of each of them

(i) Cationic detergents

(ii) Tranquillizers

(iii) Antihistamines

(3)

25. (a) An organic compound A with molecular formula $\text{C}_8\text{H}_8\text{O}$ gives positive DNP and iodoform tests. It does not reduce Tollen's or Fehling's reagent, and does not decolorise bromine water also. On oxidation with chromic acid H_2CrO_4 , it gives a carboxylic acid B with molecular formula $\text{C}_8\text{H}_6\text{O}_3$. Deduce the structure of A and B.

(b) Complete the following reactions by identifying A, B and C



(5)

26. (a) Derive the relationship between relative lowering in vapour pressure and mole fraction of the volatile liquid.
 (b) Heptane and octane form an ideal solution at 373 K, the vapour pressures of the pure liquids at this temperature are 105.2 kPa and 46.8 kPa respectively. If the solution contains 25g of heptane and 28.5 g of octane, calculate:
 (i) vapour pressure exerted by heptane
 (ii) vapour pressure exerted by solution
 (iii) mole fraction of octane in the vapour phase. (5)

Or

27. (a) Which aqueous solution has higher concentration 1 molar or 1 molal solution of the same solute. Give reasons.
 (b) 1.5 g of KCl was dissolved in 100 g of water and the solution originally at 2°C froze at -0.24°C . Calculate the percentage dissociation of the salt. K_f for water per 1000 g = 1.86°C .
 27. (a) In the titration of FeSO_4 with KMnO_4 in the acidic medium, why is H_2SO_4 used instead of HCl ?
 (b) Give reasons:
 i) Among transition metals, the highest oxidation state exhibits in oxoanions of a metal.
 (ii) Ce^{4+} is used as an oxidizing agent in volumetric analysis.
 (iii) Transition metals form a number of interstitial compounds.
 (iv) Zn^{2+} salts are white while Cu^{2+} salts are blue.

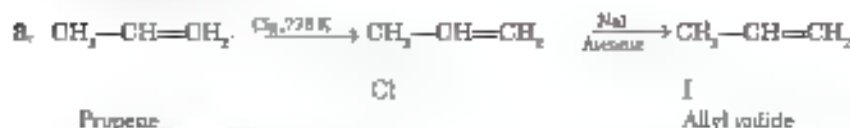
Or

- (a) Compare the chemistry of actinoids with that of the lanthanoids with special reference to:
 i) electronic configuration ii) oxidation state iii) atomic and ionic sizes
 (b) Explain the following:
 i) Of the d^1 species, Cr^{2+} is strongly reducing while Mn^{3+} is strongly oxidising.
 ii) Cobalt (II) is stable in an aqueous solution, but in the presence of complexing reagents it is easily oxidised. (3)

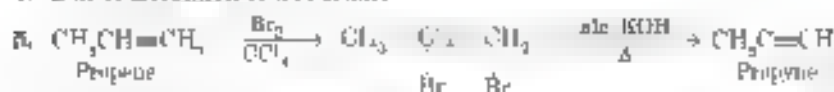
HINTS & SOLUTIONS TO UNIT PRACTICE TESTS

UNIT 10 : HALOALKANES AND HALOARENES

- $$\begin{array}{c} \text{H}_3 \quad \text{CH}_3 \\ | \quad | \\ \text{CH}_2 - \text{CH} - \text{CH} - \text{CH}_3 \\ | \\ \text{H} \end{array}$$
- 2,3-Dimethylbutane



4. Due to liberation of free iodine

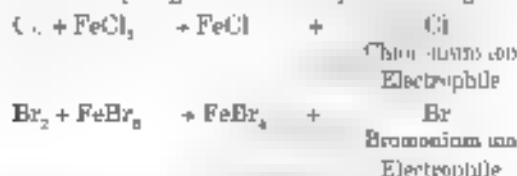


0. $\text{C}_6\text{H}_5\text{CH}_2\text{Cl}$ is a 1° alkyl halide and $\text{t}\text{-C}_4\text{H}_9\text{CHClC}_6\text{H}_5$ is a 2° alkyl halide. In S_N1 reaction, the reaction proceeds through the formation of carbocation. In the first step, the alkyl halide ionizes to give carbocation.



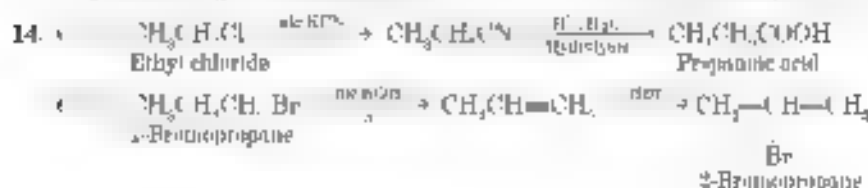
The carbocation **II** is more stable than **I** because the +ve charge on carbon can be delocalised over two adjacent rings. On the other hand, the +ve charge in carbocation **I** is delocalised over only one benzene ring. Therefore, $\text{C}_6\text{H}_5\text{CHClC}_6\text{H}_5$ can be more easily hydrolysed than $\text{C}_6\text{H}_5\text{CH}_2\text{Cl}$ in $\text{S}_\text{N}1$ reactions. However, in $\text{S}_\text{N}2$ reactions, the reactivity depends upon the steric hindrance. Therefore, $\text{C}_6\text{H}_5\text{CH}_2\text{Cl}$ will get hydrolysed more easily than $\text{C}_6\text{H}_5\text{CHClC}_6\text{H}_5$ because of less steric hindrance.

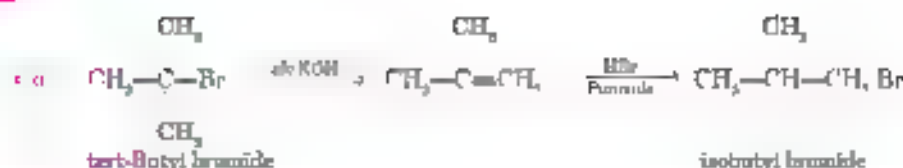
7. (i) CH_3I , because I^- ion is a better leaving group than Br^-
(ii) CH_3Cl , because of steric hindrance in case of $(\text{CH}_3)_3\text{CCl}$
8. (i) 3-Bromo-2-methyl propene
(ii) 4-Bromo-4-methylpent-2-ene
9. Lewis acids help to generate electrophile during the bromination and chlorination.



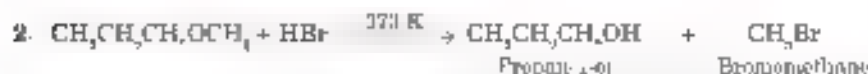
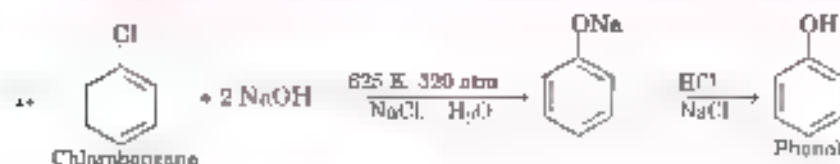
The electrophile then attacks the benzene ring to form a carbocation, which loses a proton to form aryl chloride or aryl bromide.

10. The haloalkanes are only slightly soluble in water. In order to dissolve a haloalkane in water, energy is required to overcome the attractions between the haloalkane molecules and break the hydrogen bonds between water molecules. Since less energy is released on the formation of new attractions between haloalkane and water molecules and these are not very strong as the original hydrogen bonds present in water and hence the solubility of haloalkanes is low.

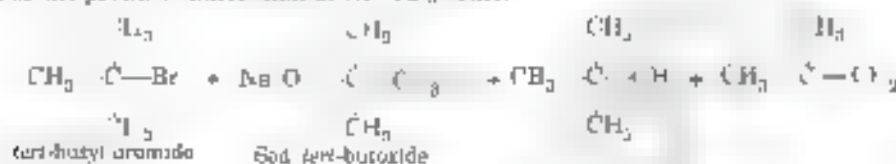




UNIT 11 : ALCOHOLS, PHENOLS AND ETHERS

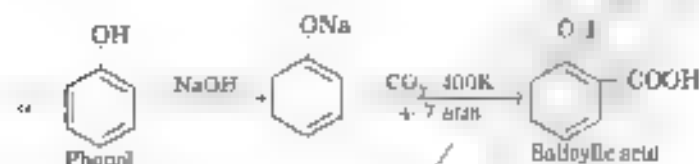


3. To prepare di-tert-butyl ether by Williamson's synthesis, we require tert-butyl iodide and sodium tert-butoxide. Since tert-butyl bromide is a 3° alkyl halide, it prefers to undergo elimination rather than substitution reaction. Therefore isobutylene is obtained as the product rather than di-tert-butyl ether.



4. α -Naphthol

5. $1^\circ > 2^\circ > 3^\circ$

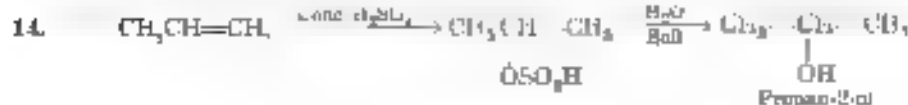
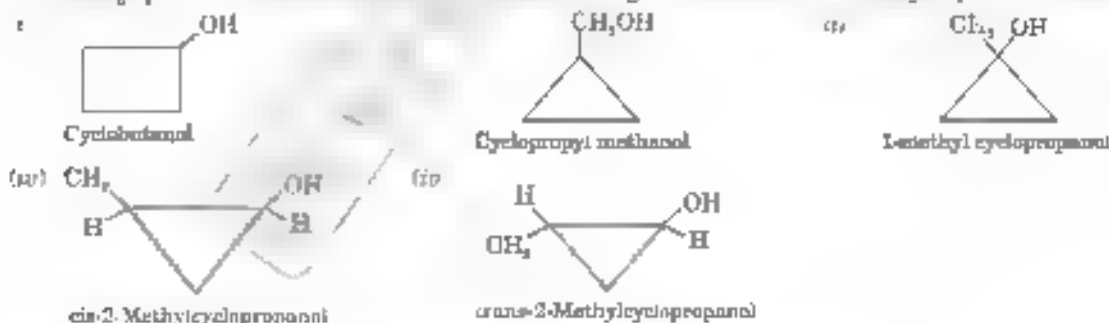


7. α -6-Dimethylphenol

8. 2-Ethoxybutane

9. Phenol, $\text{C}_6\text{H}_5\text{OH}$ is more acidic than ethanol because of greater resonance stability of phenoxide ion than phenol.

10. :



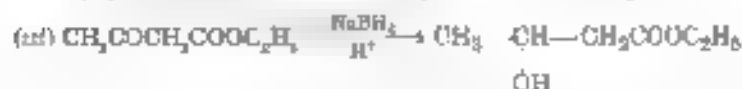
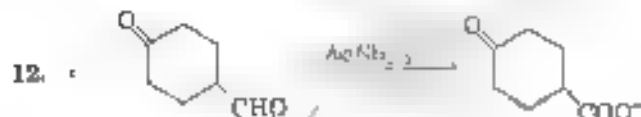
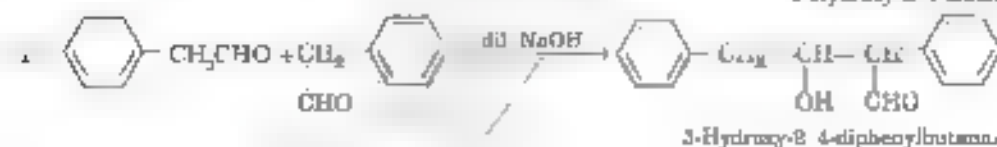
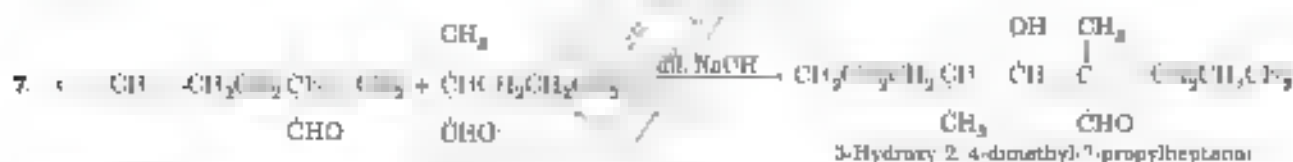
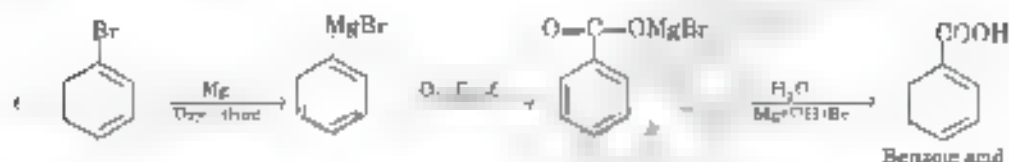
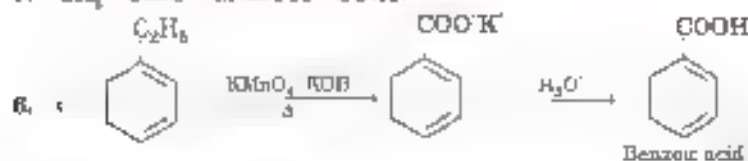
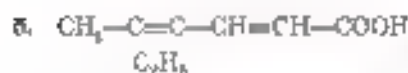


UNIT 12 : ALDEHYDES, KETONES AND CARBOXYLIC ACIDS

1. sp^3

2. $\text{C}_4\text{H}_9\text{CO}_2\text{H} < \text{C}_4\text{H}_9\text{OH} < \text{C}_4\text{H}_9\text{COOH}$

3. Rosenmund's reaction



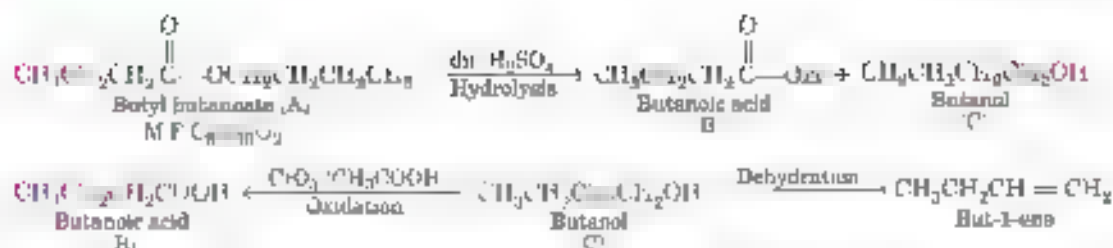
13. Since the given compound on hydrolysis with dil. H_2SO_4 gives carboxylic acid B and an alcohol C, it must be an ester. Since the oxidation of alcohol C gives the acid B, therefore, both the carboxylic acid B and alcohol C must contain same number of C atoms.

14. Since ester A contains 8 carbon atoms, therefore, both carboxylic acid (B) and the alcohol (C) must contain 4 C atoms each.

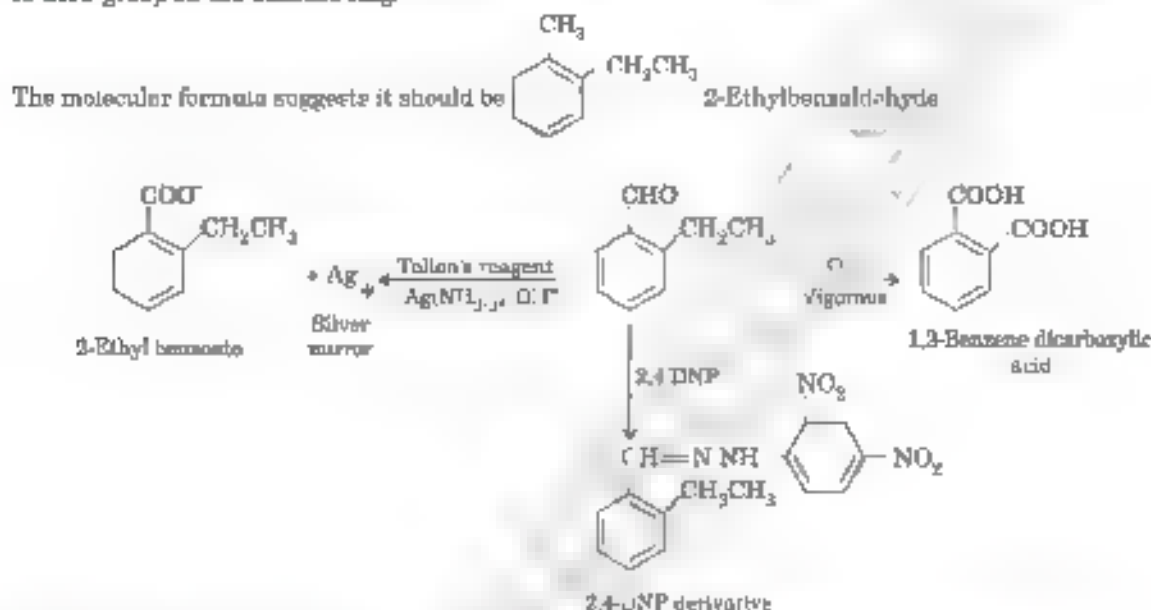
15. Alcohol C on dehydration gives but-1-ene and therefore, C must be a straight chain alcohol, i.e. butanol-1-ol.

16. B is obtained by the oxidation of C and therefore, B must be butanoic acid.

This also suggests that the ester A must be butyl butanoate. The relevant reactions are

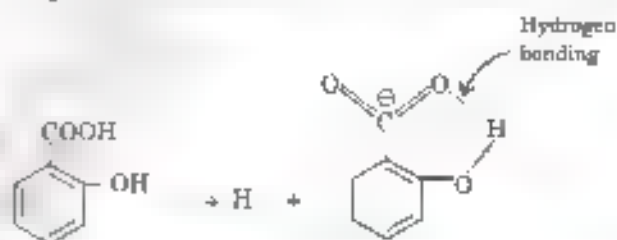


18. (a) The given compound forms 2,4-DNP derivative. Therefore it is an aldehyde or ketone. Since it reduces Tollens's reagent it must be an aldehyde. The compound undergoes Cannizzaro's reaction, so it does not contain α -hydrogen. On vigorous oxidation it gives 1,2-benzenedicarboxylic acid. It means that it must be containing alkyl group at 2-position with respect to CHO group on the benzene ring.



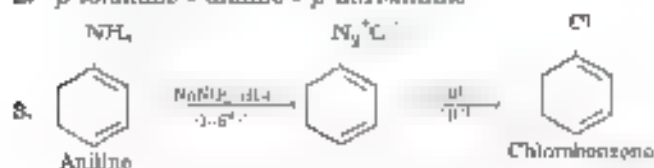
(b) butanone < Propanone < propanal < ethanal

- (c) $-\text{OH}$ group is electron releasing group and therefore it increases the negative charge on benzoate ion. As a result, *p*-hydroxy benzoate acid is less acidic than benzoic acid. However, *o*-hydroxy benzoic acid is more acidic than benzoic acid. The enhanced acidity of *o*-isomer is due to very effective intramolecular hydrogen bonding in the carboxylate ion. As a result *o*-hydroxy benzoate ion is stabilized to a great extent and therefore it makes *o*-isomer more acidic.



UNIT 13 : ORGANIC COMPOUNDS CONTAINING NITROGEN

1. N-Benzyl-N-methylbenzenamine
2. *p*-toluidine > aniline > *p*-nitroaniline

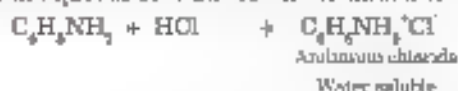


SOLUTIONS TO PRACTICE TESTS

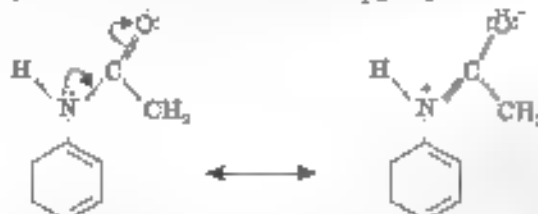
4. Amines act as nucleophiles because of the presence of a lone pair of electrons on nitrogen.



5. Aniline dissolves in aqueous HCl due to the formation of water soluble salt

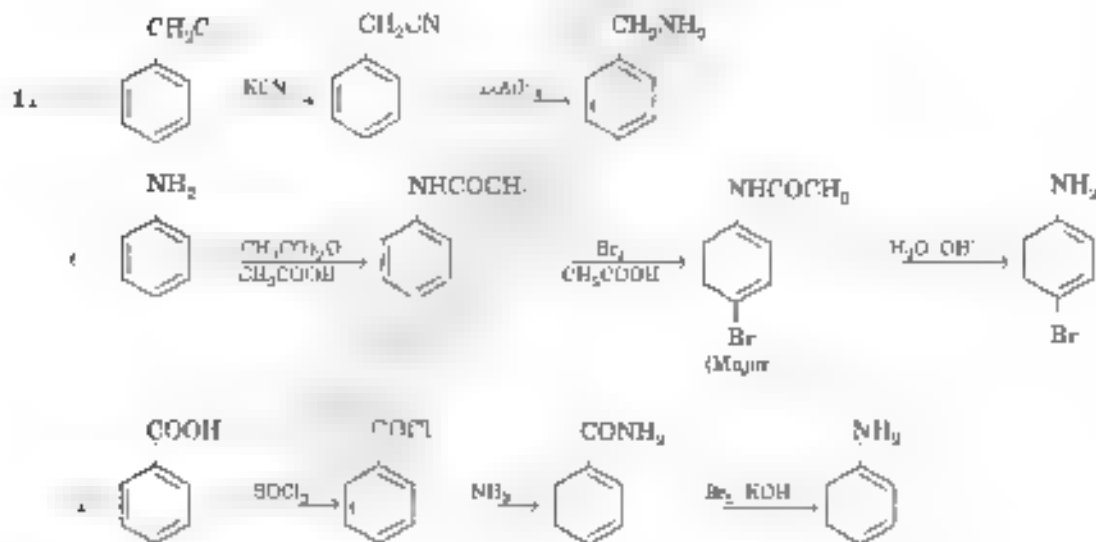
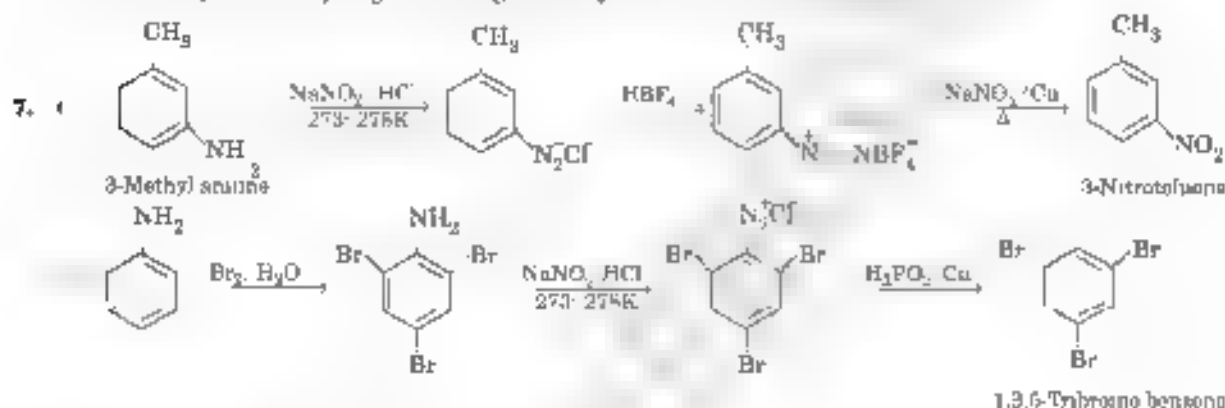


6. (i) In acetanilide, the amide group withdraws electrons from NH_2 group

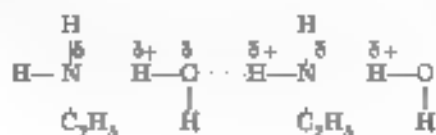


As a result, the electron pair on nitrogen gets displaced towards carbonyl group and becomes less available

- (ii) Tendency to form hydrogen bonding in methylamine is less than that in methanol.

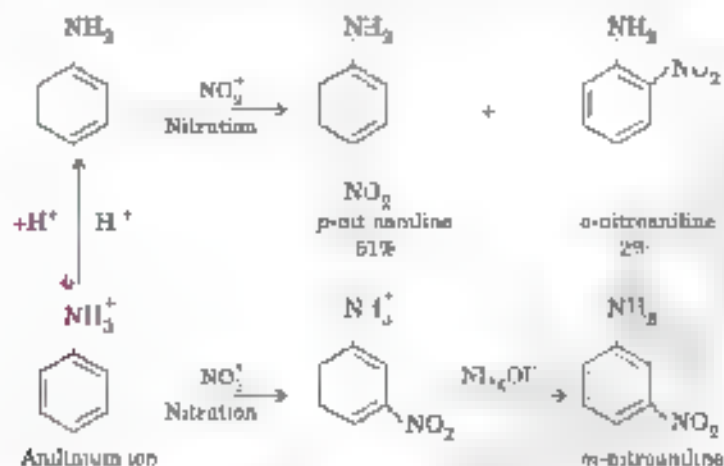


12. (a) Ethylamine dissolves in water due to intermolecular hydrogen bonding as shown below



However, because of large hydrophobic part, i.e. hydrocarbon part, of aniline, the extent of hydrogen bonding is less and therefore, aniline is insoluble in water.

- (b) Under strongly acidic conditions of nitration, in the presence of a mixture of conc. $\text{HNO}_3 + \text{H}_2\text{SO}_4$, aniline gets protonated and is converted into anilinium ion having NH_3^+ group. This group is a deactivating group and is *o*-directing. So the nitration of aniline gives *o*, *p*-nitroaniline mainly *p*-product while the nitration of anilinium ion gives *m*-nitroaniline.



Thus nitration of aniline gives a substantial amount of *o*-*p* nitroaniline due to protonation of aniline.

- (c) Aniline being a Lewis base reacts with Lewis acid such as AlCl_3 to form a salt.



As a result, N of aniline acquires +ve charge and hence it acts as a strong deactivating group for electrophilic substitution reaction. Hence aniline does not undergo Friedel Crafts reaction.

UNIT 14 : BIOMOLECULES

- Glucose and fructose
- Streptokinase
- Hydrogen bonds
- Adenine and guanine
- Amylase. It hydrolyses starch into maltose
- The bases of one strand of DNA are paired with bases of other strand through hydrogen bonding. The hydrogen bonding is very specific because structures of heterocycles allow only one mode of pairing. The two strands of DNA are complementary to each other because the sequence of bases in one strand automatically determines that of the other
- (b) (i) Gluconic acid (ii) Saccharic acid (iii) D-glucose
- (b) (i) Vitamin D
(ii) Vitamin B₁
(iii) Vitamin A
- Essential amino acids: Valine, Leucine
Non-essential amino acids: Alanine, Glycine

UNIT 15 & 16 : POLYMERS AND CHEMISTRY IN EVERYDAY LIFE

- Homopolymer
- 1,3-Butadiene $\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2$
Styrene $\text{C}_6\text{H}_5\text{CH}=\text{CH}_2$
- Polyethylene glycol sebacate $\text{CH}_2(\text{CH}_2)_n\text{COO}(\text{CH}_2\text{CH}_2)_n\text{CH}_2\text{CH}_2\text{OH}$
- 0.2% solution of phenol acts as antiseptic and 1% solution acts as disinfectant
- Bithional acts as an antiseptic agent and reduces the odours produced by bacterial decomposition of organic matter on the skin.
- These are the antibiotics which are effective against several types of harmful micro-organisms. Therefore, these are used to cure a variety of diseases. For example, chloramphenicol is effective against a variety of diseases such as typhoid, acute fever

dysentery, whooping cough, eye infections, certain urine infections, etc. Other broad spectrum antibiotics are tetracycline, rifampin, etc.

9. *c* These diminish or abolish the main actions of histamines in the body and hence prevent the allergic reactions.

These are used to relieve pains without causing impairment of consciousness, mental confusion, incoordination or paralysis or some other disturbances of nervous system e.g., aspirin.

11. Hexamethylenediamine $\text{H}_2\text{N}-(\text{CH}_2)_6-\text{NH}_2$
 Adipic acid $\text{HO}-\underset{\text{O}}{\underset{\parallel}{\text{C}}}-(\text{CH}_2)_4-\underset{\text{O}}{\underset{\parallel}{\text{C}}}-\text{OH}$
 Phenol $\text{C}_6\text{H}_5\text{OH}$
 Formaldehyde HCHO
 Tetrafluoroethylene $\text{CF}=\text{CF}$

14. *a* Drugs designed to cure some ailments in one organ in the body do not affect the other parts because they work on different receptors. For example, secretion of histamine causes allergy. It also causes acidity i.e. release of excessive hydrochloric acid in the stomach. Since anti-allergic and antacid drugs work on different receptors, therefore, antihistamines cure allergy while antacids remove acidity.

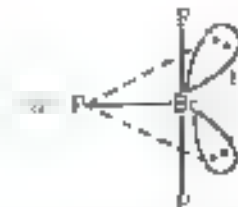
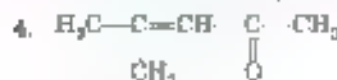
- b* Noradrenaline induces a feeling of well-being and helps in changing the mood. If the level of noradrenaline is low, then the signal sending activity of the hormone becomes low and the person suffers from depression. In such cases, the patient needs anti-depressant drugs which inhibit the enzymes which catalyse the degradation of noradrenaline. The common drugs used as anti-depressant are pramoxid and phenelzine.

MOCK TEST

COMPLETE SOLUTION

1. $[\text{Co(en)}_3]^{3+}$ because bidentate ligand ethylenediamine forms chelate which is more stable
2. Carbohydrates are generally optically active because they contain one or more chiral atoms

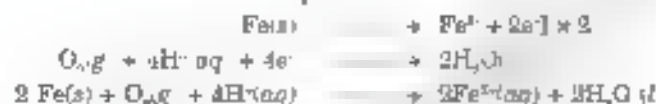
3. Saccharin or the sulphbenzimidazole



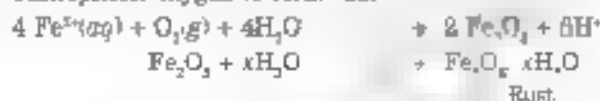
7. Oxidation

Reduction

Overall reaction



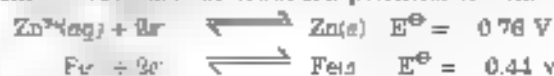
Ferrous ions are oxidised by atmospheric oxygen to form rust



Rusting of iron can be prevented by **sacrificial protection**.

In this method, iron is protected from rusting by covering it with a layer of a metal more active than iron. This prevents loss of electrons from iron. The active metal loses electrons in preference to iron and goes into ionic state. Therefore the covering metal is consumed with time but as long as it is present on the surface of iron, the latter is not rusted.

Zinc is commonly used for covering iron surfaces. The process of covering iron with zinc is called galvanization. If some scratches occur on the protective zinc film on coated iron, even then iron will not be rusted. This is due to the fact that because of scratches both zinc and iron get exposed to oxidation but zinc undergoes oxidation in preference to iron. This is so because the reduction potential of zinc is less than the reduction potential of iron.



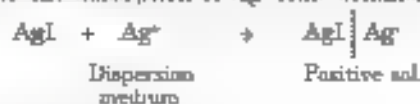
Therefore, zinc undergoes oxidation in preference to iron.

8. (a) is negative sol
(b) is positive sol

The origin of charge is the selective adsorption of ions from the dispersion medium. The particles constituting the dispersed phase adsorb preferentially only those ions which are common with their own lattice ions. For example, if silver nitrate solution is added to an aqueous solution of potassium iodide, the silver iodide formed will adsorb negative I^- ions (common ions) from the dispersion medium to form a negatively charged sol.



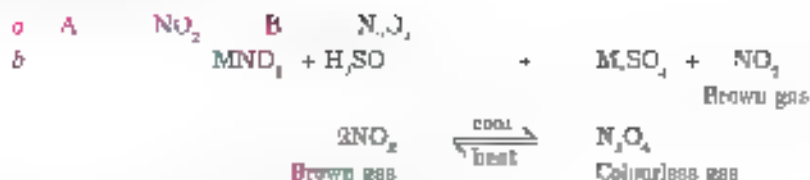
However, if silver iodide is formed by adding potassium iodide to silver nitrate solution, the sol will be positively charged due to the adsorption of Ag^+ ions (common ions) present in the dispersion medium.



9. (i) $\text{Mg}_3\text{N}_2 + 6\text{H}_2\text{O} \rightarrow 3\text{Mg}(\text{OH})_2 + 2\text{NH}_3$
(ii) $\text{POCl}_3 + 3\text{H}_2\text{O} \rightarrow \text{H}_3\text{PO}_4 + 3\text{HCl}$

(or)

The unknown compound is some metal nitrate which gives brown gas NO_2 . On cooling the gas changes to colourless gas B, which is N_2O_4 .



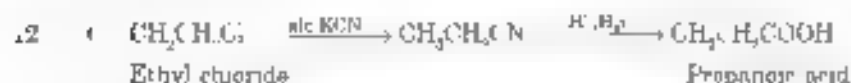
The reaction is carbylamine reaction



It is called Hoffmann degradation reaction.

11 Fuel cell. A fuel cell is a Galvanic cell in which the energy of combustion of fuels like hydrogen, methane, methanol etc. is directly converted into electrical energy

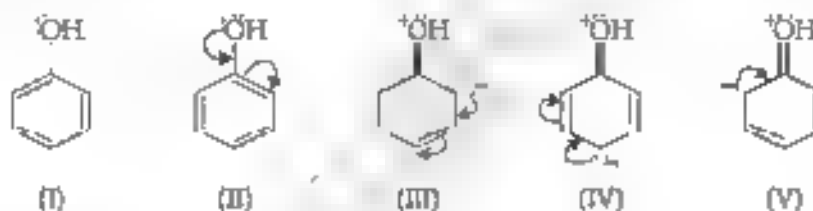
12 The molar conductivity of a solution when the concentration approaches zero is called limiting molar conductivity. It is expressed as Λ_m°



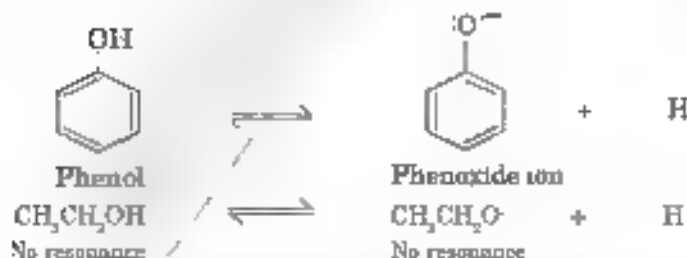
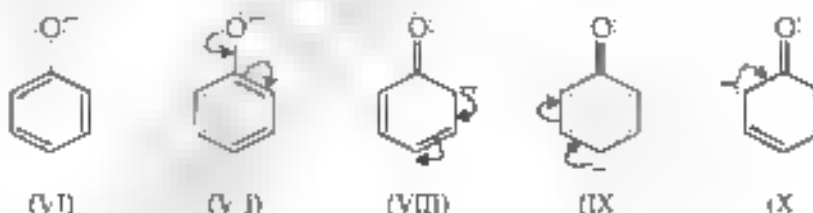
(c)

2-Chloropropane

13 (a) Phenol is more acidic than ethanol. The greater acidic character of phenol as compared to ethanol can be explained on the basis of resonance



Similarly, the phenoxide ion is resonance stabilised as follows



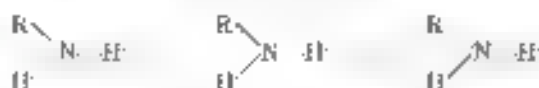
The comparison of structures of phenol and phenoxide ion shows that three structures of phenol, (II), (IV) and (V) have +ve charge on oxygen of OH group. Thus oxygen attracts the electron pair of O—H bond strongly towards itself and therefore, H can be released easily. Moreover, the phenoxide ion is more resonance stabilised than phenol. On the other hand, there is no such stability in case of ethanol as well as ethoxide ion.

b) (i) Propan-2-ol gives iodoform test but propan-1-ol does not give iodoform test.



14 Phenol gives violet colouration with neutral FeCl_3 , while cyclohexanol does not give violet colouration with neutral FeCl_3 .

- 14 a Primary amines RNH_2 have two hydrogen atoms on the N atom and therefore form intermolecular hydrogen bonding



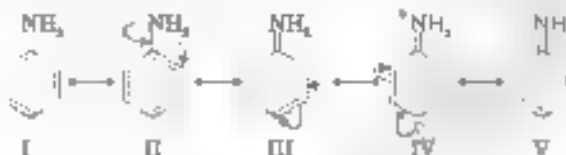
Tertiary amines R_3N do not have hydrogen atoms on the N atom and therefore these do not form hydrogen bonds. As a result of hydrogen bonding in primary amines, they have higher boiling points than tertiary amines of comparable molecular mass. For example b.p. of n-butylamine is 351 K while that of tert-butylamine is 310 K.

- 14 Both arylamines and alkylamines are basic in nature due to the presence of one pair on N atom. But arylamines are less basic than alkylamines. For example, aniline is less basic than ethylamine as shown by K_b values

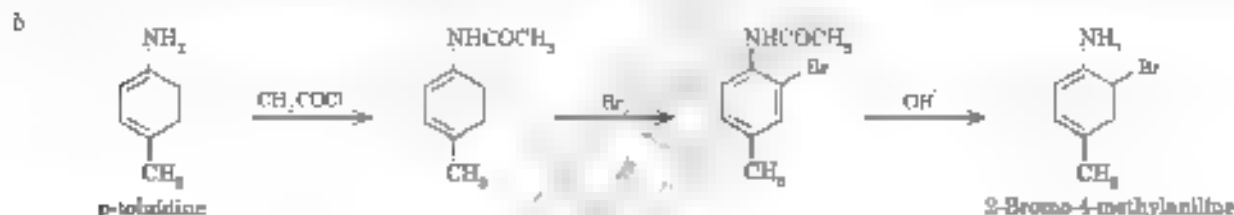
Ethylamine $K_b = 4.7 \times 10^{-4}$

Aniline $K_b = 4.2 \times 10^{-10}$

The less basic character of aniline can be explained on the basis of aromatic ring present in aniline. Aniline can have the following resonating structures



It is clear from the above resonating structures that three of these (III, IV and V) acquire some positive charge on N atom. As a result, the pair of electrons become less available for protonation. Hence, aniline is less basic than ethylamine in which there is no such resonance.



- 15 a $E = 0.81 \text{ V}$

$$E_{\text{cell}} = E^{\circ}_{\text{Ag}^+/\text{Ag}} - E^{\circ}_{\text{Mg}^{2+}/\text{Mg}}$$

$$= 0.81 - (-2.35) = 3.17 \text{ V}$$

$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - \frac{0.059}{2} \log \frac{[\text{Mg}^{2+}]}{[\text{Ag}^+]^2}$$

$$= 3.17 - \frac{0.059}{2} \log \frac{1}{(0.001)^2}$$

$$= 3.17 - \frac{0.059}{2} \times 7$$

$$= 3.17 - 0.2065 = 2.9635 \text{ V}$$

16 a $\text{Mg} \mid \text{Mg}^{2+} (0.01 \text{ M}) \parallel \text{Ag}^+ (0.0001 \text{ M}) \mid \text{Ag}$

i. Cell reaction is spontaneous

- 16 a This is because if the metal is in liquid state its entropy is higher than when it is in solid state. Therefore, the value of entropy change ΔS of the reduction process is more on +ve side when the metal formed is in the liquid state and the metal oxide being reduced is in solid state. As a result, the value of ΔG° becomes more on negative side and hence the reduction becomes easier.

- b The reduction of Cr_2O_3 with Al is thermodynamically feasible because ΔG for the reaction is negative



However, as we know, even thermodynamically favourable reaction requires some activation energy to proceed and therefore, this reaction does not occur at room temperature. Heating is required for the reaction to start.

- 16 c Fine oil is added in froth floatation method because it enhances the non-wettability of the mineral particles.

17 a $\therefore \text{Slope} = \frac{k}{2.303}$

$$\begin{aligned}
 \text{b } 2 \times 10^{-4} \text{ s}^{-1} &= \frac{k}{2.303} \\
 k &= 2 \times 10^{-4} \times 2.303 \\
 &= 4.606 \times 10^{-4} \text{ s}^{-1}
 \end{aligned}$$

∴ The rate expression for first order reaction is

$$\begin{aligned}
 kt &= 2.303 \log \frac{A_{10}}{[A]} \\
 \text{or } t &= \frac{2.303}{k} \log \frac{A_{10}}{[A]}
 \end{aligned}$$

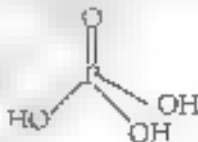
Now half life period, $t_{1/2}$ corresponds to time during which the initial concentration, A_{10} is reduced to half, i.e.

$$\begin{aligned}
 \frac{1}{2} A_{10} &= \frac{A_{10}}{2} \text{ at } t = t_{1/2} \\
 \text{or } t_{1/2} &= \frac{2.303}{k} \log \frac{A_{10}}{A_{10}/2} \\
 &= \frac{2.303}{k} \log 2 = \frac{2.303 \times 0.3010}{k} \\
 t_{1/2} &= 0.693/k
 \end{aligned}$$

18. α The acids of P which contain P—H bond are strong reducing agents. For example, both H_3PO_2 and H_3PO_3 have P—H bond and hence show reducing properties.



On the other hand, H_4PO_4 does not have P—H bond and hence does not act as reducing agent



- ∴ PCl_5 has trigonal bipyramidal geometry in which there are three P—Cl equatorial bonds and two P—Cl axial bonds. The two axial bonds are being repelled by three bond pairs at 90° while the three equatorial bonds are being repelled by two bond pairs at 90° . Therefore, axial bonds are repelled more by bond pairs than equatorial bonds and hence are longer (219 pm) than equatorial bonds (204 pm).
- α In the vapour state sulphur exists as S_8 molecules. S_8 molecule like O_2 molecule has two unpaired electrons in the antibonding molecular orbitals π^* and π^* and hence shows paramagnetism.

19. (α) $k = 6 \times 10^{-4} \text{ sec}^{-1}$, $t = 3 \text{ min} = 3 \times 60 = 180 \text{ sec}$

$$\begin{aligned}
 &= \frac{2.303}{k} \log \frac{[R]_0}{[R]} \\
 2 \times 60 \text{ sec} &= \frac{2.303}{6 \times 10^{-4}} \log \frac{0.25}{[R]} \\
 \log \frac{0.25}{[R]} &= \frac{2 \times 60 \times 6 \times 10^{-4}}{2.303} = 4.172506 \\
 \frac{0.25}{[R]} &= 1.062 \\
 [R] &= \frac{0.25}{1.062} = 0.235 \text{ M} \\
 t_{1/2} &= \frac{0.693}{6 \times 10^{-4}} = 1.155 \text{ s}
 \end{aligned}$$

$$\text{Rate} = \frac{1}{3} \times \frac{d[C]}{dt}$$

$$\therefore \text{Rate of reaction} = \frac{1}{3} \times 1.3 \times 10^{-4} = 4.33 \times 10^{-5} \text{ mol L}^{-1} \text{ s}^{-1}$$

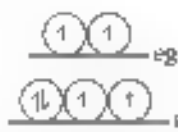
$$\therefore \text{Rate of disappearance of A} = \frac{d[A]}{dt}$$

$$\frac{1}{2} \frac{d[A]}{dt} = \frac{1}{3} \times \frac{d[C]}{dt}$$

$$\therefore \frac{d[A]}{dt} = \frac{2}{3} \frac{d[C]}{dt}$$

$$= \frac{2}{3} \times 1.3 \times 10^{-4} = 8.66 \times 10^{-5} \text{ mol L}^{-1} \text{ s}^{-1}$$

- 20 a) $[\text{FeF}_6]^{4-}$ It is a weak field complex and Fe(II) has $3d^6$ configuration. In the weak field complex Δ_o small the configuration of the complex is



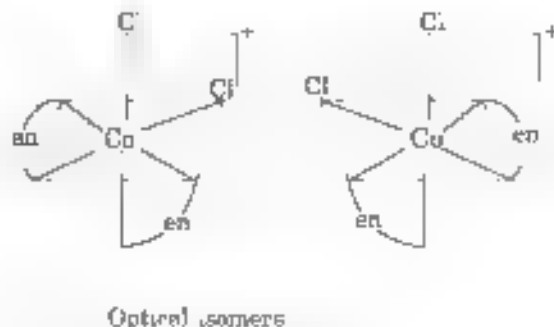
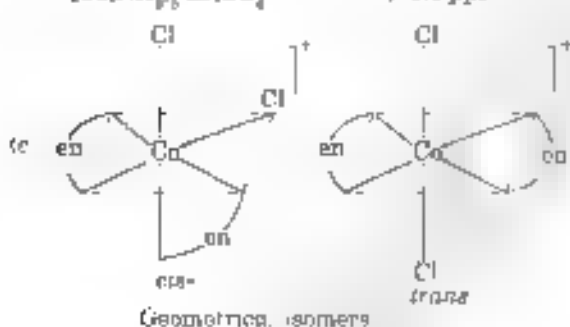
No. of unpaired electrons = 4

$[\text{Fe}(\text{CN})_6]^{4-}$ It is a strong field complex, Δ_o large and has the configuration t_{2g}^6



No. of unpaired electrons = 0

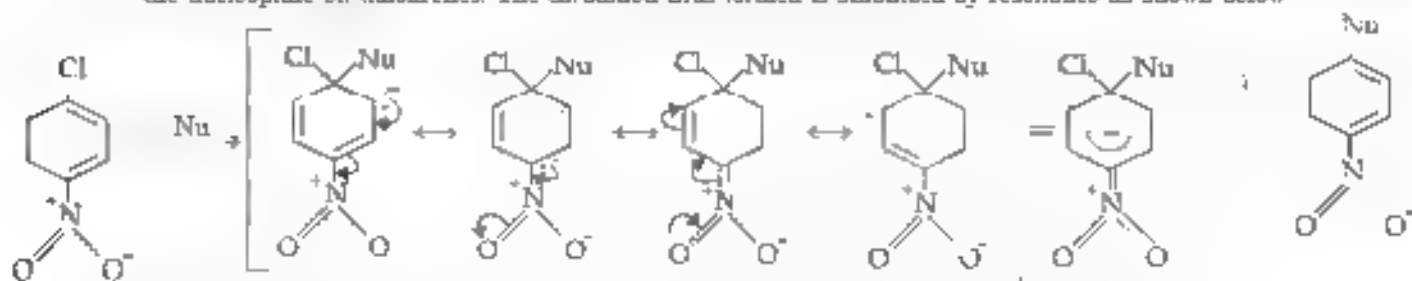
- b) These are ionisation isomers. When we treat these isomers with AgNO_3 solution, $[\text{Co}(\text{NH}_3)_5\text{SO}_4]\text{Br}$ gives yellow precipitate which indicates that Br is outside the coordination entity. $[\text{Co}(\text{NH}_3)_5\text{Br}]\text{SO}_4$ does not give yellow precipitate.



cis-form shows optical isomers

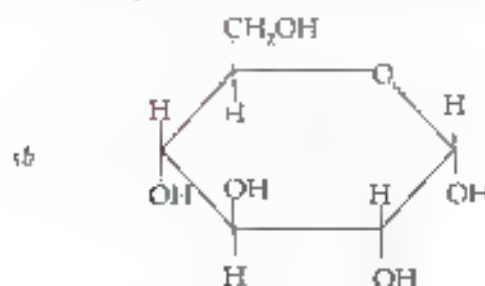
- 21 (a) 2-methyl-2-chlorobutane has higher boiling point than 1-chlorobutane because with increase in size of alkyl group, boiling point increases.

- (b) $-\text{NO}_2$ group is electron withdrawing group. It activates the *o*- and *p*-positions to the halogen atom towards nucleophilic substitution reaction. This is because it withdraws electron from the benzene ring and thus facilitates the attack of the nucleophile on haloarenes. The carbanion thus formed is stabilized by resonance as shown below.

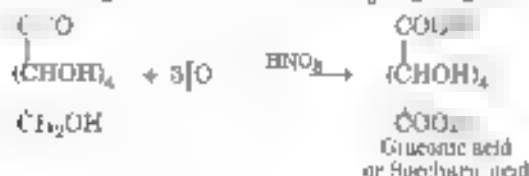


Similarly, the attack at *p*-position is also resonance stabilized. Therefore, it makes C_o reactive.

- 22 a Glucose does not give 2,4-DNP test despite of the fact that it contains —CHO group. This is because glucose does not have open chain structure.

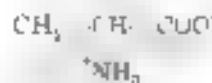


- (c) Glucose gets oxidised with HNO_3 to give gluconic acid or saccharic acid



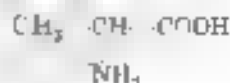
Or

In aqueous medium, amino acid $\text{CH}_2\text{CH}(\text{COOH})\text{NH}_2$ exists as dipolar ion formed by migration of a proton from carboxylic acid group to amino group as



It is called dipolar ion or zwitter ion.

- (i) In acidic medium, it exists as cationic form



- (ii) In alkaline medium, the compound A exists in anionic form as



Therefore, it migrate towards anode in electric field

- 23 a Thermoplastics are the polymers which can be easily softened repeatedly on heating and hardened on cooling. Therefore, these can be used again and again. For example,

- (i) polythene (ii) polyvinyl chloride

Thermosetting polymers are those which undergo permanent change on heating.

They become hard and infusible on heating and cannot be softened again. For example,

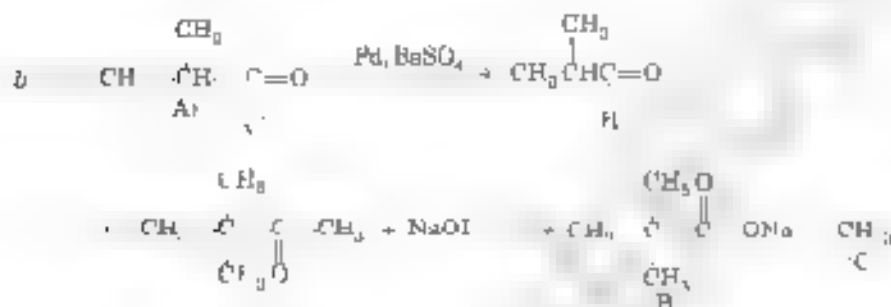
- (i) Bakelite (ii) Melamine formaldehyde.

- b 1,3-Butadiene $\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2$ and



24. **Cationic detergents** are those which have cationic hydrophobic group. These are mostly acetates, chlorides or bromides of quaternary ammonium salts.
For example, cetyltrimethyl ammonium chloride, $[\text{CH}_3(\text{CH}_2)_{15}\text{N}^+(\text{CH}_3)_3] \text{Cl}^-$
25. **'Tranquillizers'** are substances used to relieve mental diseases. They reduce tension and anxiety. They act on higher centres of nervous system and are constituents of sleeping pills.
For example, Equanil.
- Antihistamines** are drugs used to treat allergy such as skin rashes, conjunctivitis, rhinitis.
For example, Diphenylhydramine.

25. a. The given organic compound gives positive DNP test so it may be aldehyde or ketone.
i) It gives positive iodoform test, it should be methyl ketone.
ii) It does not reduce Tollen's reagent or Fehling reagent, it must be a ketone.
iii) The molecular formula, $\text{C}_9\text{H}_8\text{O}$ indicates high degree of unsaturation, yet it does not decolourise Br_2 water and hence suggests the presence of unsaturation due to aromatic ring.
iv) Drastic oxidation with chromic acid gives a carboxylic acid B with molecular formula $\text{C}_7\text{H}_6\text{O}$ and it should be benzoic acid. Therefore the compound A is mono substituted aromatic methyl ketone. The molecular formula of A suggests it to be acetophenone as



26. a. Refer Text Book.

b. Moles of heptane = $\frac{25.0}{110} = 0.23$
Moles of octane = $\frac{25.5}{114} = 0.23$
 $x_{\text{heptane}} = \frac{0.25}{0.25 + 0.25} = 0.5$
 $x_{\text{octane}} = \frac{0.25}{0.25 + 0.25} = 0.5$

Vapour pressure of heptane in solution = $105.2 \times 0.5 = 52.6 \text{ kPa}$

(i) Vapour pressure of octane in solution = $46.8 \times 0.5 = 23.4 \text{ kPa}$

Total vapour pressure of solution = $52.6 + 23.4 = 76.0 \text{ kPa}$

(ii) Mole fraction of octane in vapour phase = $\frac{23.4}{76.0} = 0.305$

Or

- a. Molar solution is more concentrated. A molar solution contains one mole of the solute present in one litre or 1000 mL of solution. On the other hand, a molal solution contains one mole of the solute in 1000g of water. At room temperature density of water is slightly less than one so that the volume of water corresponding to 1000 g will be greater than 1000 mL. $\text{Vol} = \text{mass}/\text{density} > 1$. So, the volume of water containing one mole of solute will be more in case of molar solution than molal solution. Therefore, molar solution is more concentrated than molal solution.

- b. Let us first calculate the observed molar mass as

$$M_B = \frac{K_f \times w_B \times 1000}{\Delta T_f \times w_A}$$

$$w_B = 0.5 \text{ g}, w_A = 100 \text{ g}, \Delta T_f = 0 - (-0.24) = 0.24^\circ \text{C}, K_f = 1.86$$

$$M_B = \frac{1.98 \times 0.5 \times 1000}{0.24 \times 100} = 38.75$$

$$\text{Normal molar mass of KCl} = 39 + 35.5 = 74.5$$

Van t Hoff factor

$$= \frac{\text{Normal molar mass}}{\text{Observed molar mass}} = \frac{74.5}{38.75} = 1.92$$

KCl dissociates as



If α is the degree of dissociation, then

$$\text{Initial moles} \quad 1 \quad 0 \quad 0$$

$$\text{Moles after dissociation} \quad 1 - \alpha \quad \alpha \quad \alpha$$

$$\text{Total number of moles after dissociation} = 1 - \alpha + \alpha + \alpha = 1 + \alpha$$

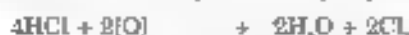
$$= \frac{\text{Observed moles of solute}}{\text{Normal moles of solute}} = \frac{1 + \alpha}{1}$$

$$\frac{1 + \alpha}{1} = 1.92 \quad \text{or} \quad 1 + \alpha = 1.92$$

$$\text{or} \quad \alpha = 1.92 - 1 = 0.92$$

Degree of dissociation = 92%

- 27 a This is because a part of oxygen produced from KMnO_4 will be used up to oxidise HCl to Cl_2



- b Oxometal ions have highest oxidation state e.g. Cr^{6+} in CrO_4^{2-} has an oxidation state of +6 while Mn in MnO_4^- has an oxidation state of +7. This is because of combination of metal with oxygen which is highly electronegative and oxidising element.

- c $\text{Ce}^{4+}/\text{Ce}^{3+}$ has E° value of 1.74V which suggests that Ce^{4+} can act as an oxidising agent.

- iii Transition metals have a unique character to form interstitial compounds with small non-metallic elements such as hydrogen, boron, carbon and nitrogen. The small atoms of these non-metallic elements (H, B, C, N etc) fit into the vacant spaces of the lattices of the transition metal atoms. As a result of the fitting up of the interstitial spaces, the transition metals become rigid and hard. These interstitial compounds have similar chemical properties as the parent metals but have different physical properties, particularly density, hardness and conductivity. For example, steel and cast iron are hard because of the formation of interstitial compounds with carbon.

These interstitial compounds have variable composition and cannot be expressed by a simple formula. Therefore, these are called non-stoichiometric compounds.

- v Zn^{2+} has $3d^{10}$ configuration while Cu^{2+} has $3d^9$ configuration. Therefore Zn^{2+} does not have vacant $3d$ subshell and hence is not coloured, whereas Cu^{2+} has vacant $3d$ subshell and therefore electron can be promoted from t_{2g} to e_g orbitals by absorption of light. Hence it is blue in colour.

(or)

- a **Electronic configurations.** The general electronic configuration of lanthanoids is $[\text{Xe}]4f^{0-14} 5d^{0-2} 6s^2$ whereas that of actinoids is $[\text{Rn}]5f^{0-14} 6d^{0-2} 7s^2$. Thus, lanthanoids involve the filling of $4f$ -orbitals.

- a **Oxidation states.** Lanthanoids have principal oxidation state of +3. In addition, the lanthanoids show limited oxidation states such as +2, +3 and +4 because of large energy gap between $4f$ and $5d$ subshells. On the other hand, actinoids show a large number of oxidation states because of small energy gap between $5f$ and $6d$ subshells.

- v **Atomic and ionic sizes.** Both lanthanoids and actinoids show decrease in size of their atoms or ions on +3 oxidation state. In lanthanoids, the decrease is called lanthanoid contraction and is not made it as called actinoid contraction.

- b E° values for $\text{Cr}^{3+}/\text{Cr}^{2+}$ is negative (-0.41V) and for Mn^{2+}/Mn is positive ($+1.57\text{V}$). Thus Cr^{3+} can undergo oxidation and, therefore, is reducing agent. On the other hand, Mn^{2+} can undergo reduction, and therefore, acts as an oxidising agent.

- c In the presence of complexing agents, cobalt gets oxidised from +2 to +3 state because $\text{Co}(\text{NH}_3)_6^{3+}$ is more stable than $\text{Co}(\text{NH}_3)_6^{2+}$.

APPENDICES

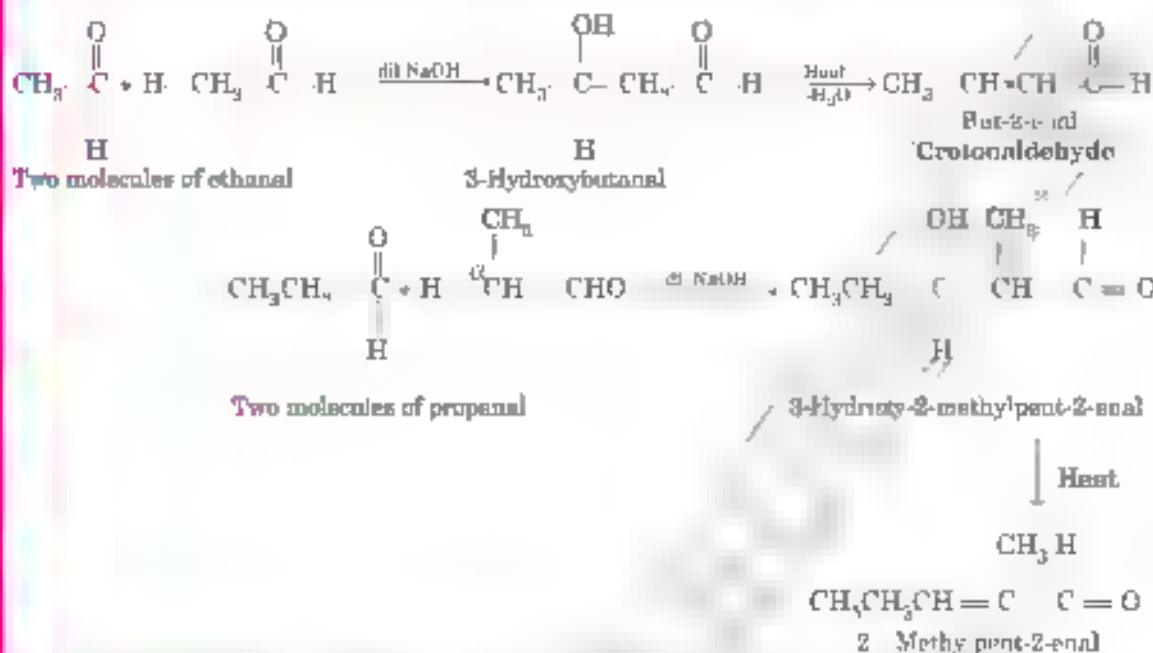
- A. **Important Name Reactions**
- B. **Distinction between Some Pairs of Organic Compounds (Chemical Tests)**
- C. **Organic Conversions**
- D. **Problems Based upon Organic Reactions**

APPENDIX-A

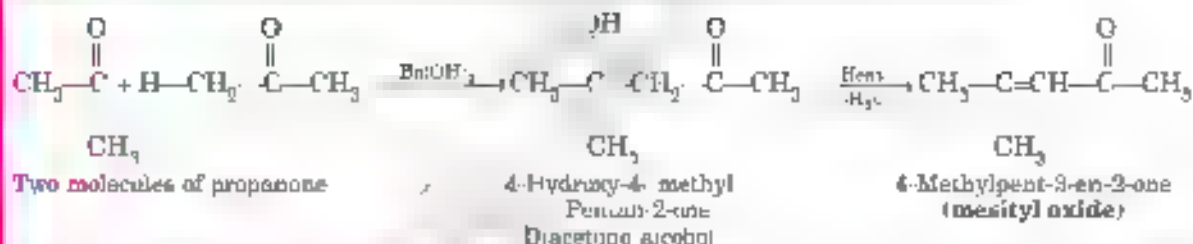
Important Name Reactions

1 Aldol condensation

Two molecules of α -dehydes or ketones containing α -hydrogen atom, in the presence of dilute alkali (i.e. NaOH, $\text{Ba}(\text{OH})_2$ etc.) undergo condensation to form β -hydroxy aldehydes or β -hydroxy ketones.



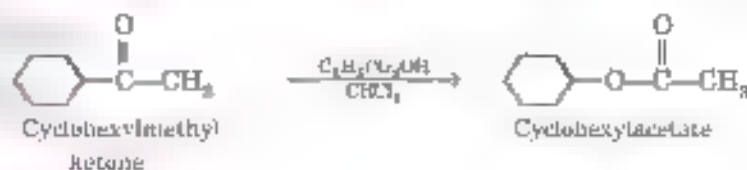
* Please note this reaction. The second molecule comes only from α -carbon atom.



Formaldehyde and benzaldehyde which do not have α -hydrogen atom do not undergo aldol condensation.

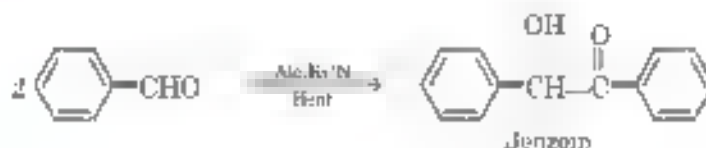
2 Baeyer Villiger Oxidation of Ketones

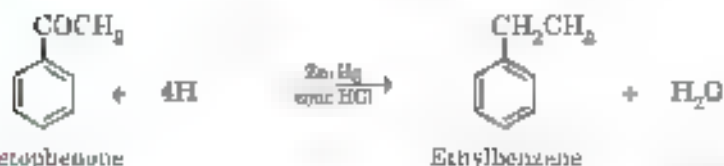
Ketones react with peroxo acid to form esters. In this reaction, the oxygen from the peroxy acid is inserted between the carbonyl group and one of the attached carbons of the ketone to give an ester.



3 Benzoin condensation

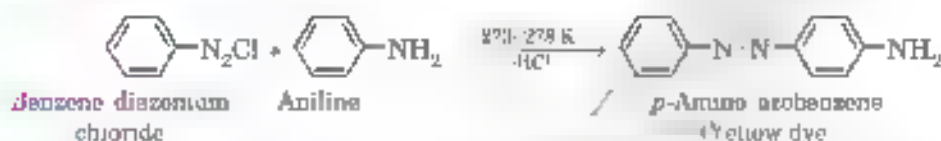
Two molecules of aromatic α -dehydes such as benzaldehyde on heating in the presence of ethanolic KCN get condensed to form benzoin.



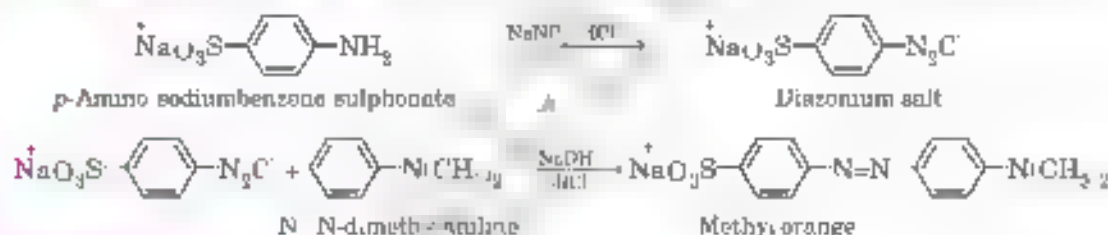


18 Coupling reaction

The reaction of diazonium salts with phenols and aromatic amines to form azo compounds. The reaction is carried out in cold solution.

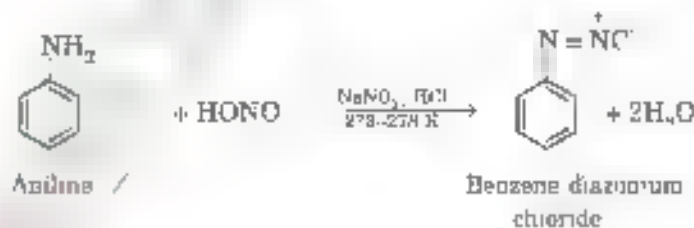


Methyl orange which acts as an indicator in the acid-base titration is obtained by coupling the diazonium salt of *p*-aminosodiumbenzene sulfonate with *N,N*-dimethylaniline in the presence of alkali.



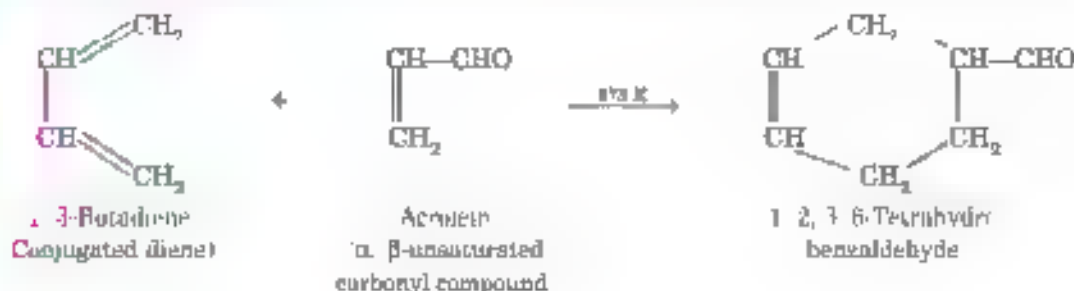
11 Diazotisation reaction

The formation of diazonium salt from primary amine on dilute mineral acid HCl or H_2SO_4 and treatment with cold solution of nitrous acid N.N.O. + HCl at 273-276K.



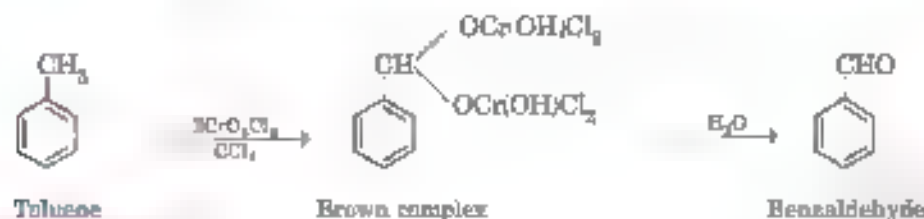
12 Diels-Alder reaction

The reaction between α, β -unsaturated carbonyl compound and a conjugated diene to form an addition product is known as **Diels-Alder reaction**. This reaction is also known as **cyclo addition**.



13 Elard's reaction

The oxidation of toluene to benzaldehyde with chromyl chloride (CrO_2Cl_2) dissolved in CCl_4 or CS_2 .

**14 Esterification reaction**

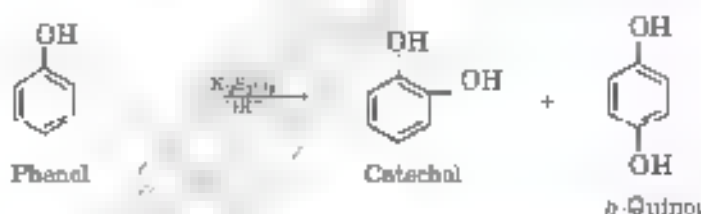
The reaction of alcohols with carboxylic acids in the presence of a few drops of conc. H_2SO_4 to form esters.



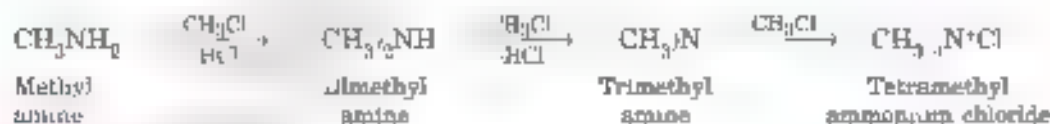
It may be noted that if HCl gas is used as a catalyst in the above reaction, the reaction is known as **Fischer-Speier** esterification.

15 Elb's reaction

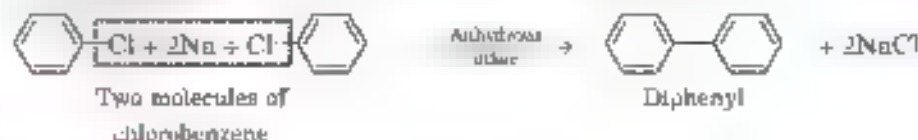
The oxidation of phenol by potassium persulphate ($\text{K}_2\text{S}_2\text{O}_8$) in alkaline medium to form a mixture of catechol and *p*-quinol.

**16 Exhaustive alkylation**

The process of converting an amine (1°, 2° or 3°) into a quaternary ammonium salt in treatment with excess of alkyl halide is called exhaustive alkylation. If alkyl halide is methyl iodide, the process is called **exhaustive methylation**.

**17 Fittig's reaction**

This reaction is a modification of the Wurtz reaction. In this reaction, two molecules of haloarene combine with metallic sodium in the presence of anhydrous ether to give diphenyl.

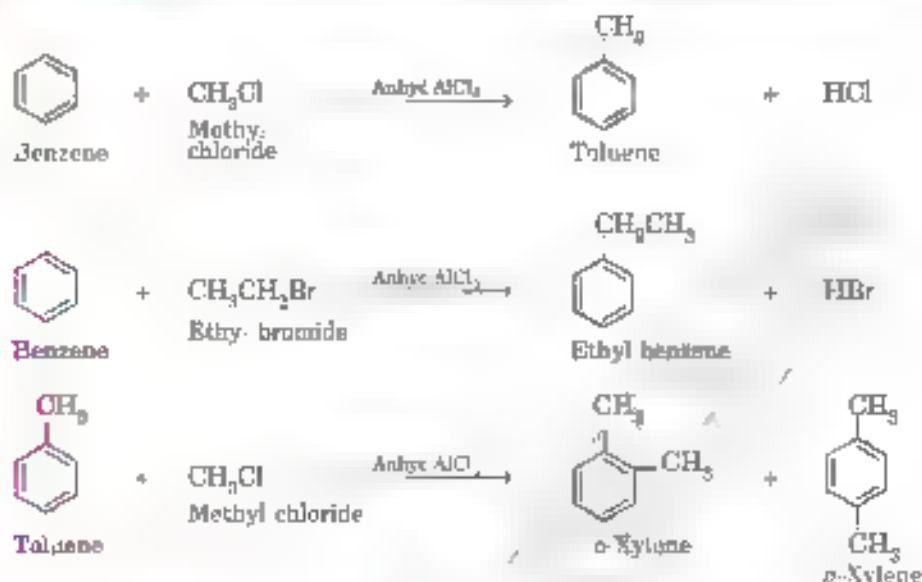
**18 Finkelstein reaction**

Chloroalkanes or bromoalkanes are converted into corresponding iodoalkanes by treating with sodium iodide dissolved in acetone.

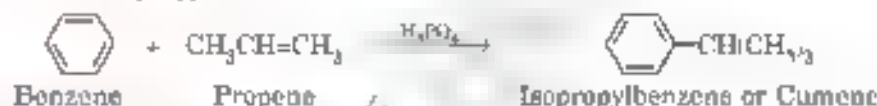


19 Friedel Craft's alkylation

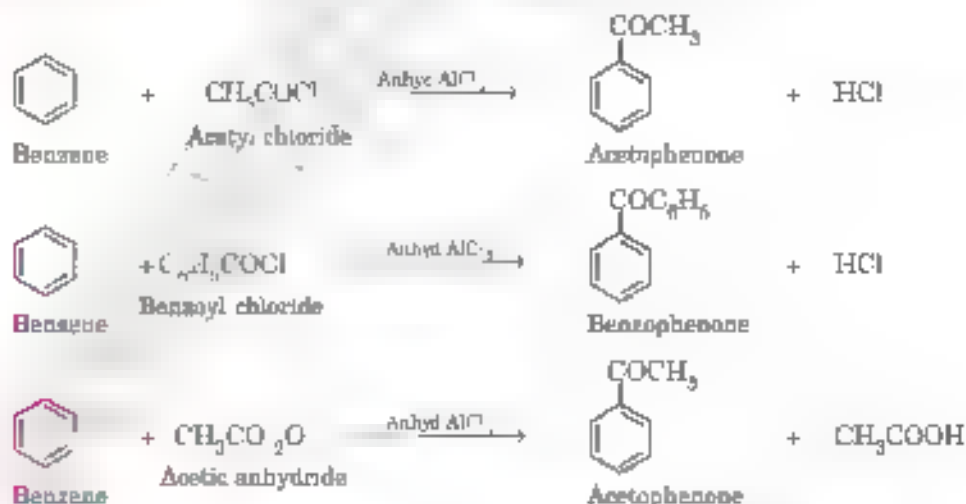
Benzene and other aromatic compounds react with alkyl halides in the presence of anhydrous AlCl_3 to form alkyl benzene. This reaction involves the addition of alkyl R group to the benzene ring.



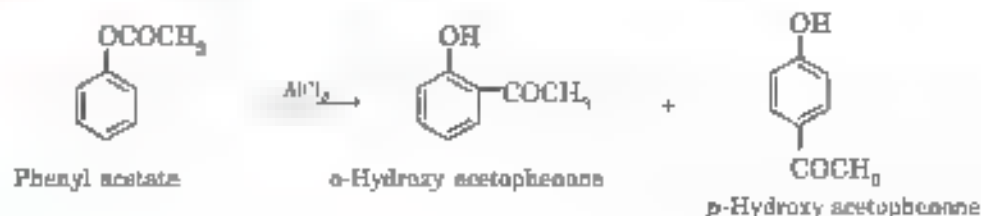
The alkylation of benzene can also be carried with propene in the presence of phosphoric acid as the catalyst when the product formed is isopropyl benzene.

**20 Friedel Craft's acylation**

Benzene and other aromatic compounds react with acid chlorides or anhydrides in the presence of anhydrous AlCl_3 to form ketones. This reaction involves the addition of acyl RCO- group.

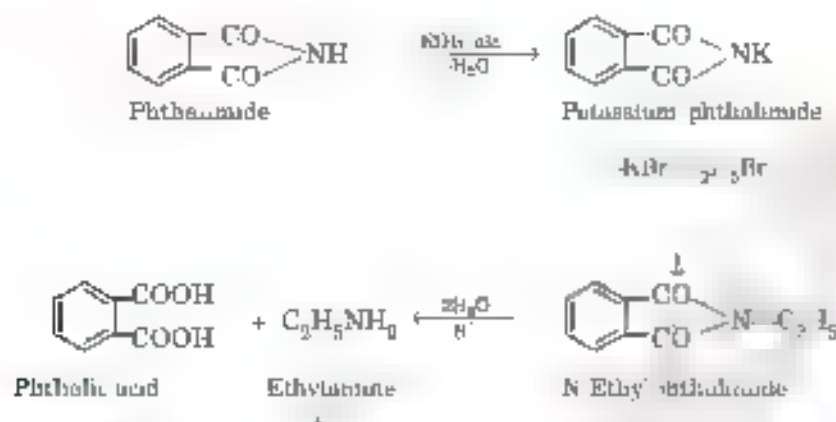
**21 Fries rearrangement**

The conversion or rearrangement of an aryl ester into *o*- and *p*-hydroxy ketone or a mixture of both by treatment with anhydrous AlCl_3 .



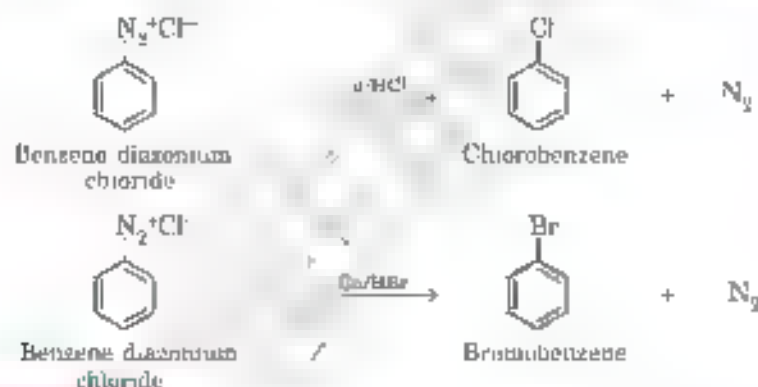
22 Gabriel phthalimide synthesis

This reaction is used to prepare primary amines. In this reaction phthalimide is converted into its potassium salt by treating with alcoholic solution of KOH. The salt is then treated with alkyl halide to give N-alkyl-phthalimide which on hydrolysis with dilute hydrochloric acid gives a primary amine as the product.



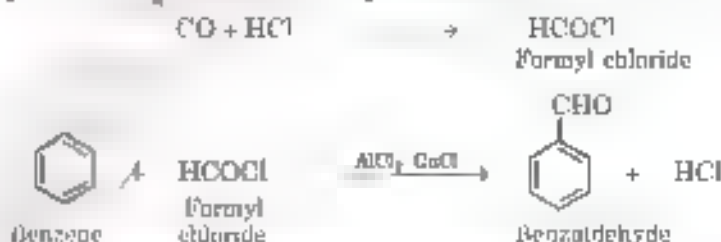
29 Gattermann reaction

This is a mild variation of Sandmeyer's reaction. This involves the reaction of benzene diazonium chloride with Cu/HCl and Cu/HBr to prepare chlorobenzene and bromobenzene respectively.



24 Gattermann Koch reaction

Benzene is converted to benzaldehyde by passing a mixture of carbon monoxide and hydrochloric acid gas in the presence of anhydrous AlCl_3 and traces of cuprous chloride



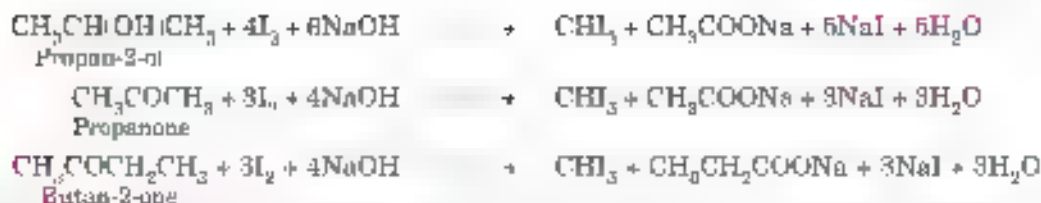
This reaction is, thus, a modification to the Friedel-Craft reaction in which $-\text{CHO}$ group is introduced in the benzene ring.

25 Halofarm reaction

The compound containing methyl group bonded to carbonyl group i.e. methyl ketones $\text{CH}_3\text{CO-}$ or the compounds which can be converted to methyl ketones upon oxidation e.g. $\text{CH}_3\text{CH}_2\text{-}$ react with aqueous sodium

carbonate and iodine solution and give yellow precipitates of iodoform. This reaction is also called **iodoform reaction**

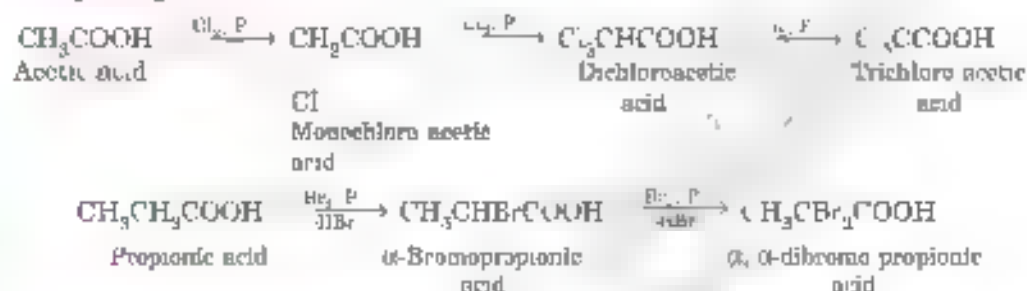




This reaction is commonly used to distinguish between methyl ketones or methyl carbinols from other ketones and alcohols.

26 Hell Volhard Zelinsky reaction

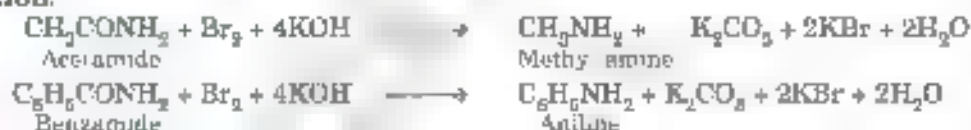
The aliphatic carboxylic acids containing α -hydrogen react with Cl_2 or Br_2 in the presence of a small amount of red phosphorus to give α -haloacids. With excess of halogen, all the α -hydrogen atoms of the aliphatic carboxylic acids are replaced by halogen atoms.



The α -halogen in the reaction can be replaced by other groups such as $-\text{OH}$, $-\text{CN}$, $-\text{NH}_2$, $-\text{COOH}$, etc. by suitable reagents.

27 Hoffmann bromamide reaction

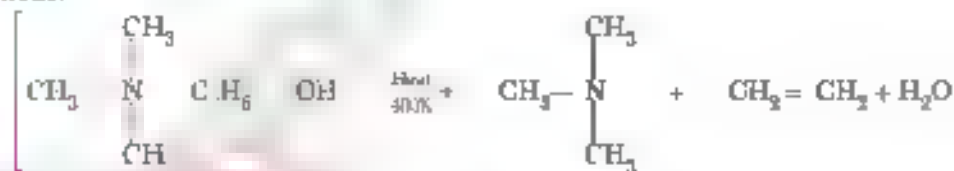
The amides can be converted into primary amines containing one carbon atom less than the original amide by heating with a mixture of Br_2 in the presence of NaOH or KOH . This reaction is also called **Hoffmann's degradation reaction**.



The reaction is very useful to convert a higher member in a family to its next lower member.

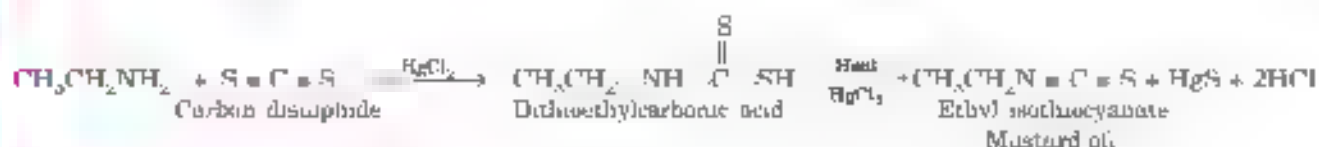
28 Hoffmann elimination reaction

This is the pyrolysis of quaternary ammonium hydroxide which contains one alkyl group other than methyl to give alkene.



29 Hoffmann mustard oil reaction

When a mixture of primary amine, carbon disulphide and mercuric chloride is heated, alkyl isothiocyanate with a characteristic smell of mustard oil is formed.



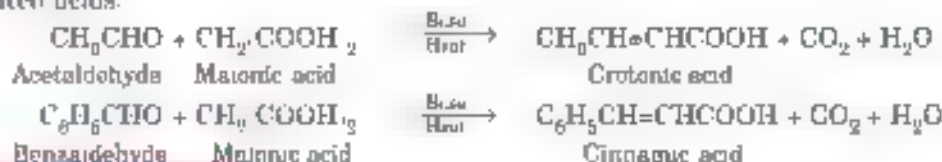
30 Hunsdiecker reaction

Alkyl halides are prepared by decomposing the silver salts of carboxylic acids dissolved in CCl_4 by bromine or chlorine.

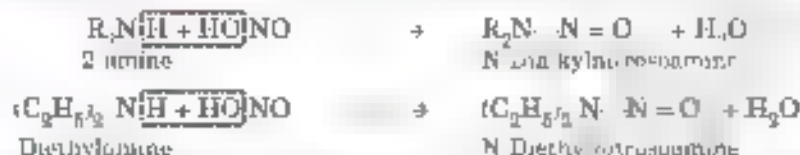


94 Knoevenagel reaction

Aldehydes react with compounds containing active methylene group in the presence of organic bases and form α , β -unsaturated acids.

**95 Libermann nitroso reaction**

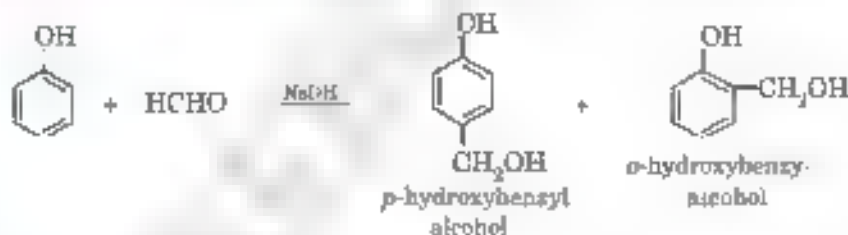
Both aliphatic and aromatic secondary amines react with nitrous acid $\text{NaNO}_2 + \text{HCl}$ to give *N*-nitroso amines which are generally yellow oily compounds and are insoluble in mineral acids.



The nitrosamine on warming with a crystal of phenol and a few drops of concentrated sulphuric acid gives a green solution which upon treatment with aqueous alkali solution changes to deep blue. This reaction is used as a test to distinguish secondary amines from primary and tertiary amines.

96 Lederer-Mannasse reaction

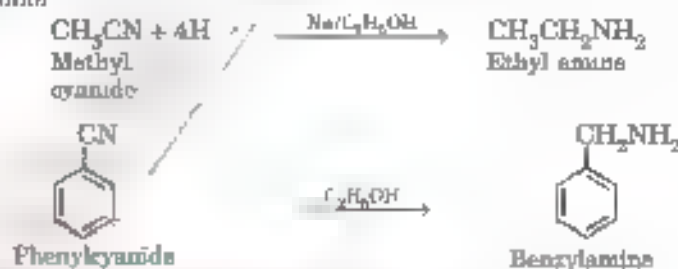
Phenol condenses with aliphatic or aromatic aldehydes in the *o*- and *p*-positions. For example, phenol undergoes condensation with formalin (40% aqueous formaldehyde) at low temperature to form *p*-hydroxy benzyl alcohol.



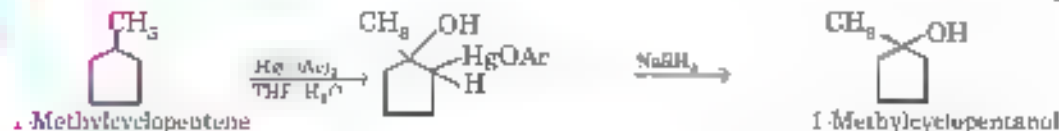
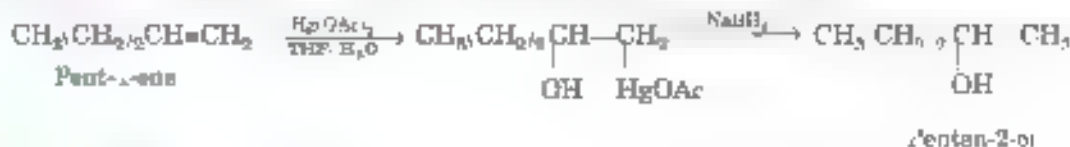
This reaction is the basis of preparation of bakelite.

97 Mendius reaction

The nitrile or aryl cyanide is reduced to a primary amine with nascent hydrogen produced by the action of sodium amalgam and alcohol.

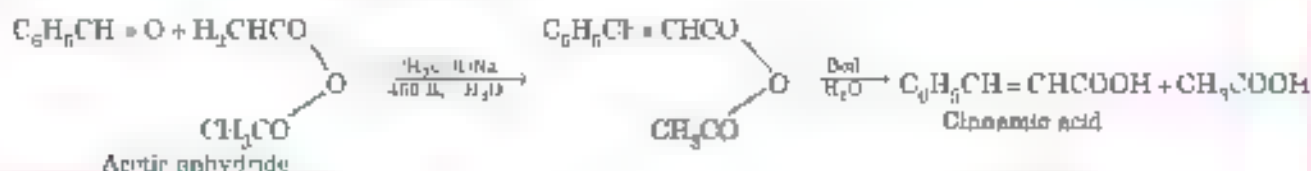
**98 Oxymercuration and demercuration of alkenes**

Alkenes react with mercuric acetate in a mixture of THF and water to give hydroxyalkyl mercury compound involving addition of $-\text{OH}$ and HgOAc to the double bond. This is called **Oxymercuration**. Then NaBH_4 reduces HgOAc and replaces with hydrogen. This is **demercuration**.



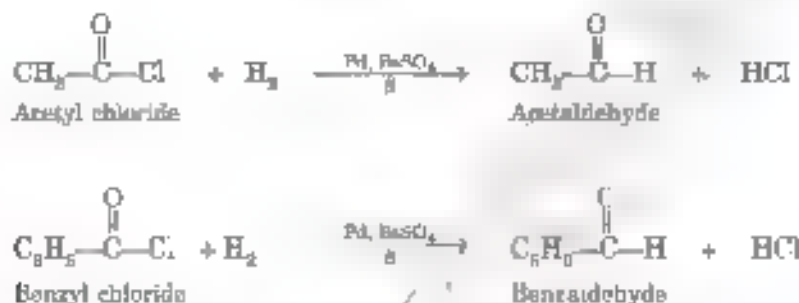
50 Perkin's reaction

Benzaldehyde on heating with acetic anhydride in the presence of sodium acetate, and the hydrolysis of the product obtained gives α , β -unsaturated acid, cinnamic acid



48 Rosenmund's reaction

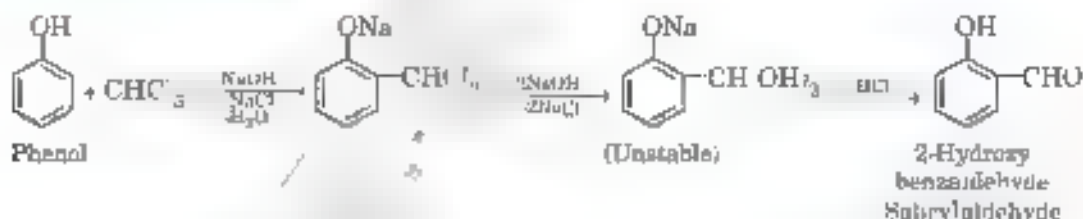
Acid chlorides are converted to corresponding aldehydes by catalytic reduction. The reaction is carried out by passing through a hot solution of the acid chloride in the presence of palladium deposited over barium sulphate partially poisoned with sulphur or quinoline.



The poisoning of palladium catalyst decreases its activity and it does not allow the further reduction of aldehyde into alcohol.

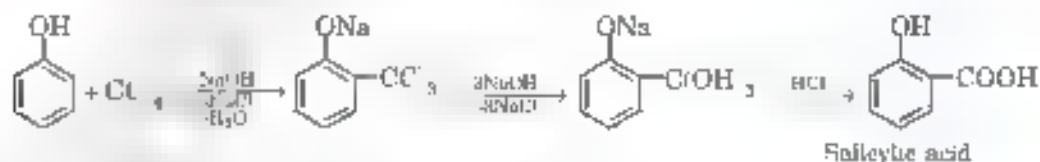
Reimer-Tiemann reaction

Phenols react with chloroform in the presence of aqueous alkali at 340 K. The hydrolysis of the resulting product gives 2-hydroxybenzaldehyde (salicylaldehyde).



In this reaction, a small amount of *p*-hydroxy benzaldehyde is also formed

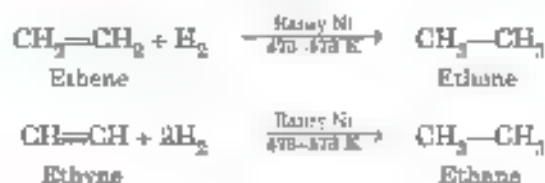
If instead of chloroform carbon tetrachloride is used, salicylic acid is formed.



A small amount of *p*-hydroxy benzoic acid will also be formed.

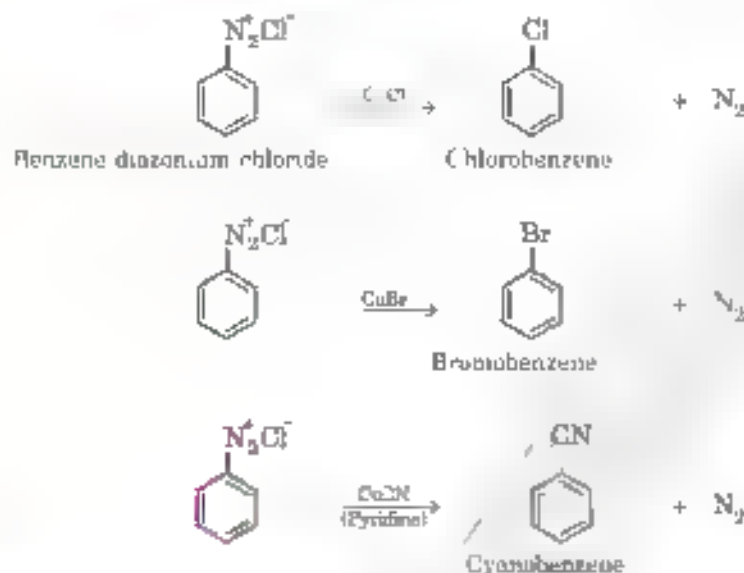
Sabatier and Sendern's reaction

Unsaturated hydrocarbons are reduced to saturated hydrocarbons with hydrogen in the presence of Raney nickel as catalyst at 473-573 K.

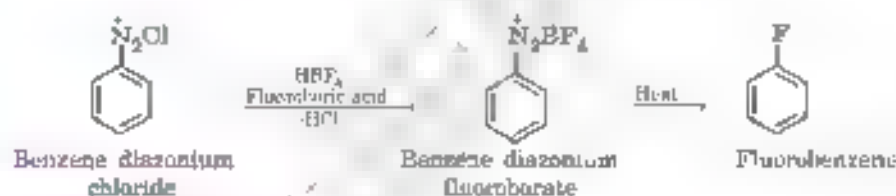


43 Sandmeyer's reaction

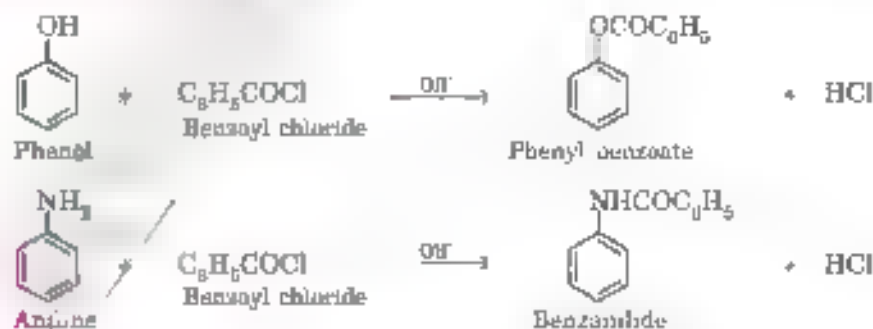
Benzene diazonium chloride is converted to chlorobenzene, bromobenzene, cyanobenzene on treatment with CuCl/HCl , CuBr/HBr and CuCN/KCN respectively.

**44 Schiemann reaction**

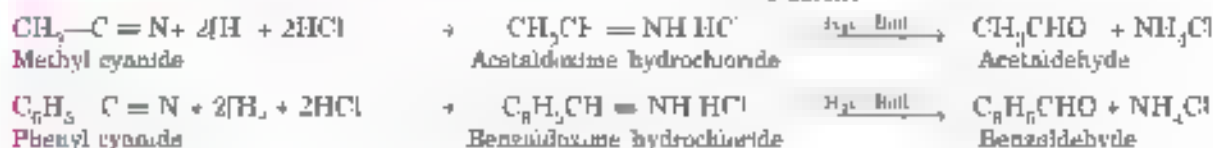
Fluorobenzene is prepared from benzene diazonium chloride by treating with fluoroboric acid and heating the product formed.

**45 Schotten-Baumann reaction**

The reaction involves the benzoylation of phenol, primary or secondary amine with benzoyl chloride in the presence of aqueous sodium hydroxide.

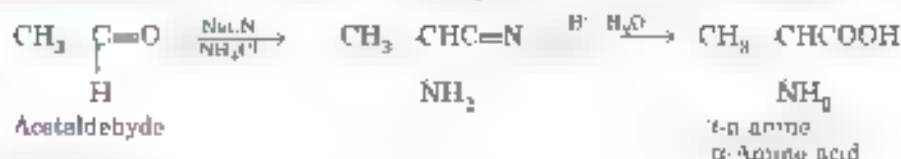
**46 Stephen's reaction**

The partial reduction of alkyl nitriles even leads to the corresponding aldehydes with a suspension of anhydrous SnCl_2 in ether saturated with HCl at room temperature followed by hydrolysis.

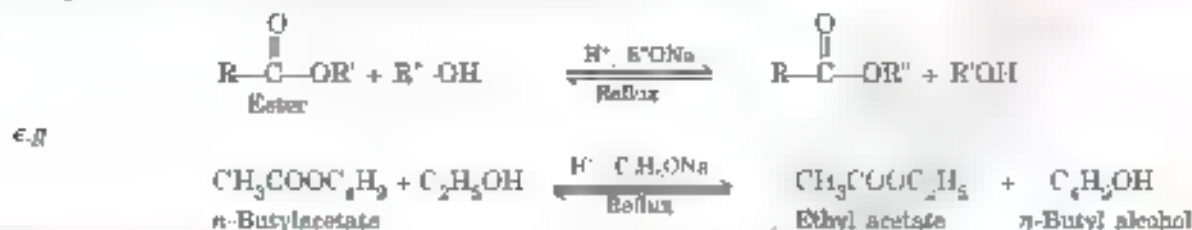


47 Strecker's synthesis

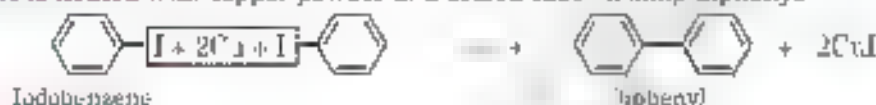
The reaction involves the conversion of an aldehyde to an α -amino acid with one more carbon atom

**48 Transesterification**

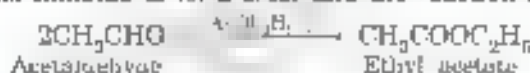
When an ester is treated with excess of another alcohol, other than one from which ester is formed, in the presence of a base such as the corresponding sodium or potassium alkoxide or an acid H_2SO_4 or HCl as catalysts, a new ester and a new alcohol is formed

**49 Ullmann reaction**

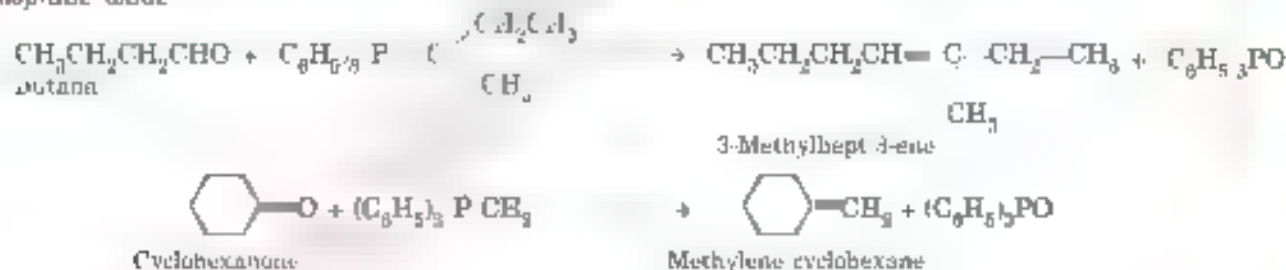
Iodobenzene is heated with copper powder in a sealed tube forming diphenyl

**50 Tischenko reaction**

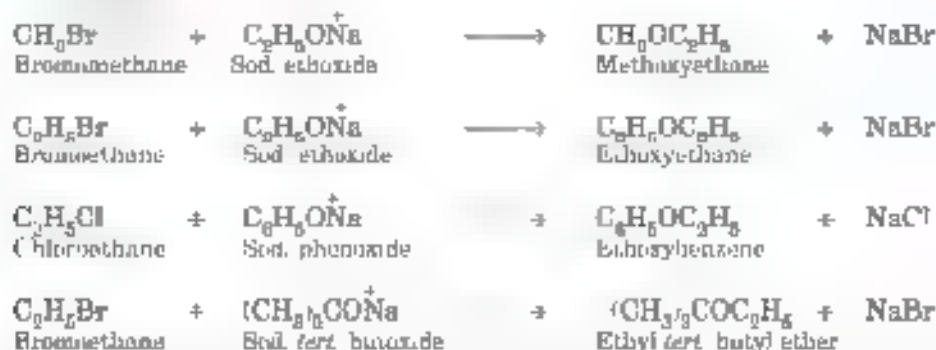
Aldehydes can be made to undergo Cannizzaro's reaction with alkoxide. Under these conditions the acid and the alcohol combine to form ester and the reaction is known as Tischenko reaction

**51 Wittig reaction**

Aldehydes and ketones react with phosphoranes or phosphorous ylides to give alkenes and triphenylphosphine oxide

**52 Williamson synthesis**

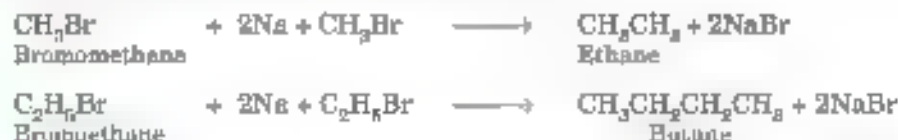
This reaction is used to prepare both symmetrical and unsymmetrical ethers by treating alkyl halides with either sodium alkoxide or sodium phenoxide



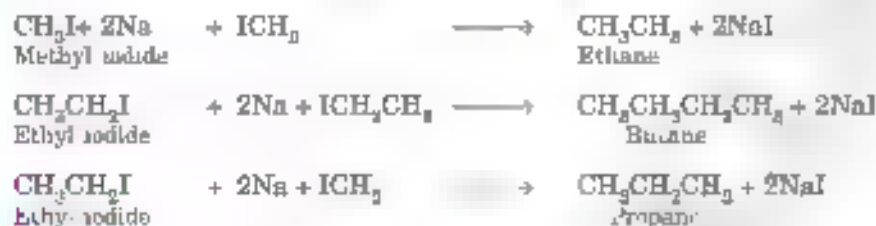
Alkyl halides cannot be used for the preparation of alkyl aryl ethers because of their low reactivity

63 Wurtz reaction

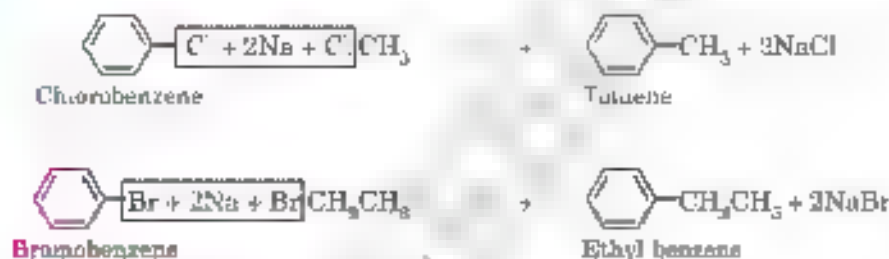
Alkyl halides react with metallic sodium in the presence of anhydrous ether to form alkanes. This reaction is used for the preparation of higher alkanes. For example,



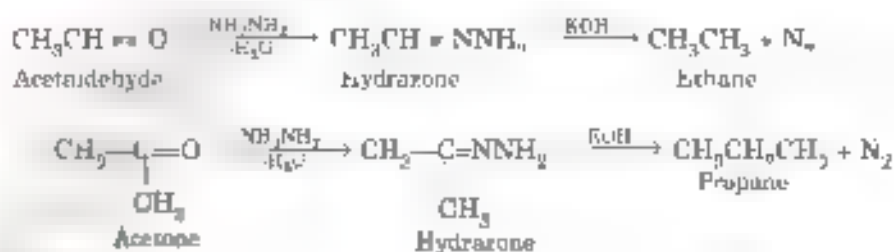
If we start with different alkyl halides, then a mixture of alkanes will be formed. For example, if we start with CH_3I and $\text{C}_2\text{H}_5\text{I}$, a mixture of ethane, propane and butane will be formed.

**64 Wurtz Fittig reaction**

Halobenzene reacts with haloarenes in the presence of sodium in anhydrous ether to form alkyl benzenes.

**65 Wolff-Kishner reduction**

The reduction is done by heating the carbonyl compound with a mixture of hydrazine and KOH in the presence of ethylene glycol. It is called **Wolff-Kishner reduction**.

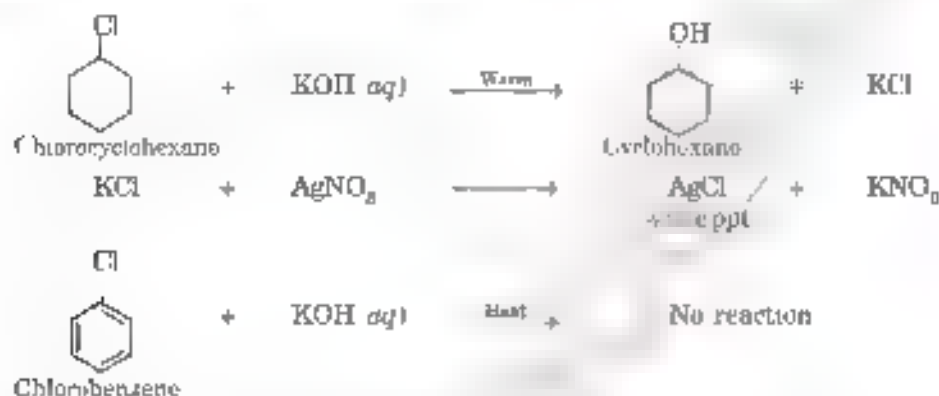


APPENDIX B

Distinction between Some Pairs of Organic Compounds (Chemical Tests)

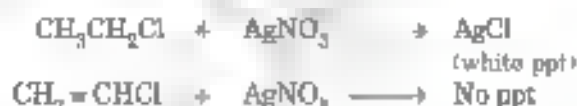
1. Chlorobenzene (C_6H_5Cl) and Chlorocyclohexane Add a small quantity of aqueous KOH to each compound. Acidify with dil HNO_3 and add silver nitrate solution.

Chlorocyclohexane gives *white ppt* while chlorobenzene does not give this test

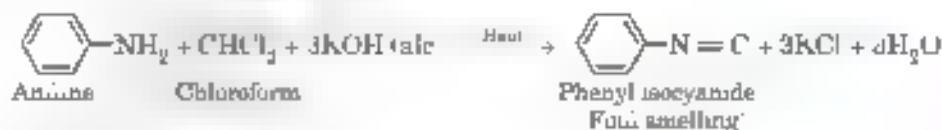


2. Chlorobenzene and Benzyl chloride Same as 1. Benzyl chloride reacts with alcoholic $AgNO_3$ solution to give white ppt of $AgCl$ while chlorobenzene does not give this test.

3. Ethyl chloride (C_2H_5Cl) and Vinyl chloride ($CH_2=CHCl$) Ethyl chloride reacts with $AgNO_3$ solution to give white ppt of $AgCl$ while vinyl chloride does not give this test



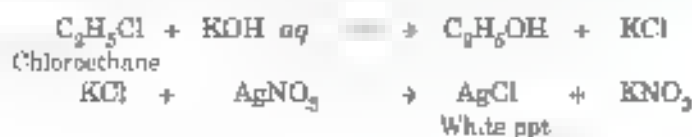
4. Carbon tetrachloride and Chloroform When chloroform is heated with aniline and alcoholic KOH solution, foul smell of isocyanide carballymine is produced.



Carbon tetrachloride does not give this test

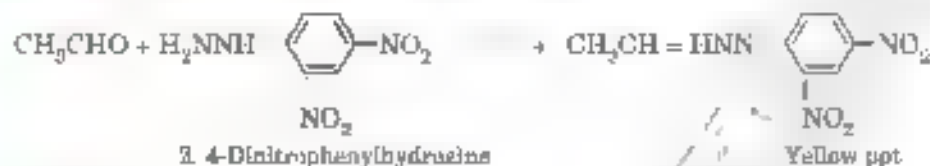
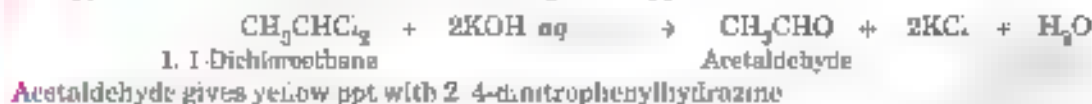
5. Chlorobenzene and n-Hexyl chloride Same as answer 1. n-Hexyl chloride reacts with alcoholic $AgNO_3$ solution to give white ppt of $AgCl$ while chlorobenzene does not give this test.

6. Chloroethane and Bromoethane Add a small amount of aqueous KOH to each compound. Acidify with dil HNO_3 and add a few drops of $AgNO_3$ solution. A white ppt, insoluble in NH_4OH , indicates chloroethane. A faint yellow ppt, partially soluble in NH_4OH , indicates bromoethane.

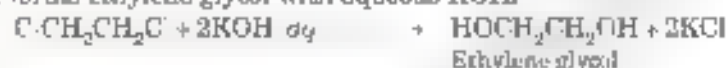




7. 1, 1-Dichloroethane (gem dihalide) and 1, 2-Dichloroethane (Vic-dihalide) Add aqueous KOH solution to each compound, warm and add a few drops of 2, 4-dinitrophenyl hydrazine. 1, 1-Dichloroethane forms a yellow ppt while 1, 2-dichloroethane does not give the ppt.



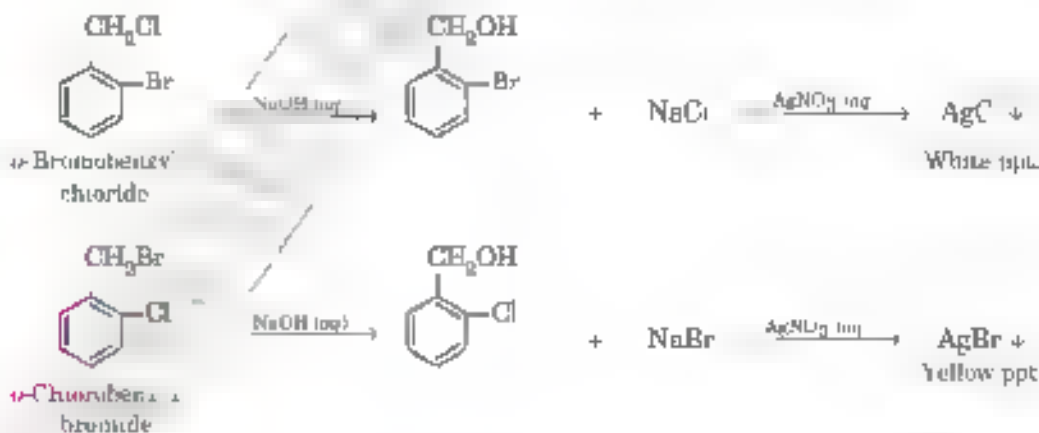
1, 2-Dichloroethane forms ethylene glycol with aqueous KOH.



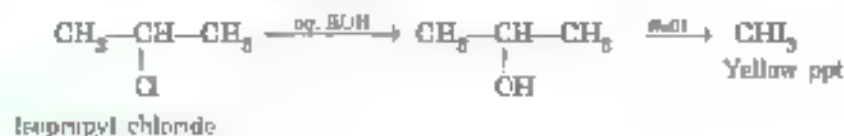
Ethylene glycol does not give ppt with 2, 4-dinitrophenyl hydrazine.

8. 2-Bromopropene (allyl bromide) and 1-Bromopropane (n-alkyl bromide) Add a small amount of dilute alkaline KMnO_4 solution (Baeyer's reagent) to each compound and shake. 2-Bromopropene $\text{CH}_2=\text{CHCH}_2\text{Br}$ decolorises pink colour of KMnO_4 while 1-bromopropane $\text{CH}_3\text{CH}_2\text{CH}_2\text{Br}$ does not give this test.

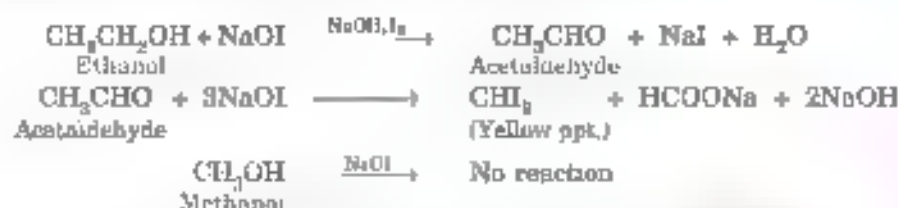
9. o-Bromobenzyl chloride and o-Chlorobenzyl bromide o-Bromobenzyl chloride on shaking with aqueous NaOH and subsequent treatment with aqueous AgNO_3 gives white precipitate of AgCl . On the other hand, o-chlorobenzyl bromide on shaking with aqueous NaOH and subsequent treatment with aqueous AgNO_3 produces a yellow ppt of AgBr .



10. n-Propylchloride and Isopropyl chloride Isopropyl chloride on alkaline hydrolysis with aqueous KOH gives isopropyl alcohol which gives yellow ppt with NaOI (Iodoform test). n-Propyl alcohol on hydrolysis with aq. KOH gives n-propyl alcohol which does not give iodoform test.



11. Methanol (CH_3OH) and Ethanol ($\text{CH}_3\text{CH}_2\text{OH}$) Ethanol gives iodoform test yellow ppt of CHI_3 whereas methanol does not give iodoform test



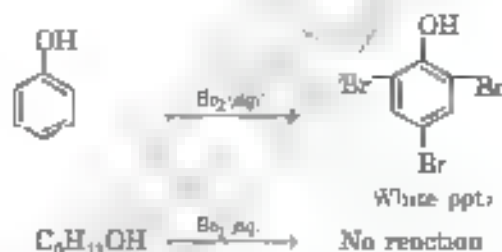
12. Ethanol ($\text{CH}_3\text{CH}_2\text{OH}$) and Benzyl alcohol ($\text{C}_6\text{H}_5\text{CH}_2\text{OH}$) Same as 11 Ethanol gives iodoform test whereas benzyl alcohol does not give iodoform test

13. Ethanol ($\text{CH}_3\text{CH}_2\text{OH}$) and Phenol ($\text{C}_6\text{H}_5\text{OH}$)

- i. Ethanol gives iodoform test whereas phenol does not give yellow ppt. of iodoform (same as 11)
- ii. Phenol reacts with neutral FeCl_3 solution to give purple colour whereas ethanol does not give any colour with neutral FeCl_3 solution.
- iii. Phenol gives coloured dye with acid solution of benzene diazonium chloride whereas ethanol does not give any dye

14. Phenol ($\text{C}_6\text{H}_5\text{OH}$) and Cyclohexanol ($\text{C}_6\text{H}_{11}\text{OH}$)

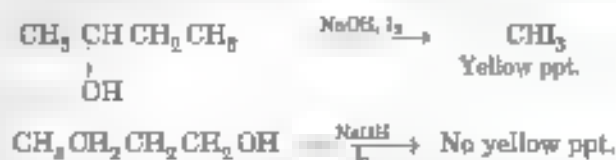
- i. Phenol gives violet colouration with neutral FeCl_3 while cyclohexanol does not give (same as 13).
- ii. Phenol gives coloured dye with benzene diazonium chloride whereas cyclohexanol does not (same as 13).
- iii. Phenol readily decolourises bromine water giving a white ppt. of 2,4,6-tribromophenol. But cyclohexanol does not



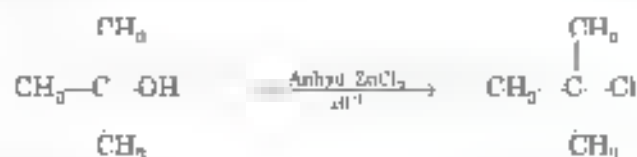
15. Propan-1-ol ($\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$) and Propan-2-ol ($\text{CH}_3)_2\text{CHOH}$) : Propan-2-ol gives iodoform test but propan-1-ol does not (same as 11).



16. Butan-1-ol and Butan-2-ol Butan-2-ol contains CH_3CHOH group and gives yellow ppt. with NaOH, I_2 Iodoform test. On the other hand butan-1-ol does not give yellow ppt. with NaOH, I_2 Iodoform test.

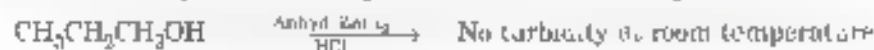


17. Propan-1-ol and 2-methylpropan-2-ol : 2-Methylpropan-2-ol reacts with Lucas reagent (anhyd. $\text{ZnCl}_2 + \text{HCl}$) giving turbidity immediately



Turbidity appears immediately

Propan-1-ol does not produce turbidity at room temperature with Lucas reagent



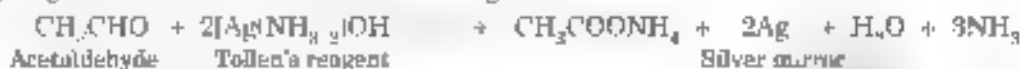
18. Formaldehyde and Acetaldehyde Acetaldehyde gives yellow ppt of iodoform with an alkaline solution of iodine (iodoform)



Formaldehyde does not give this test.

19. Acetaldehyde (Propanal) and Acetone (Propanone)

(i) Acetaldehyde gives silver mirror with Tollen's reagent.



Acetone does not give this test.

(ii) Acetaldehyde gives red ppt with Fehling solution.



20. Benzaldehyde and Acetaldehyde Acetaldehyde gives yellow ppt with an alkaline solution of iodine (iodoform test) while benzaldehyde does not give ppt.



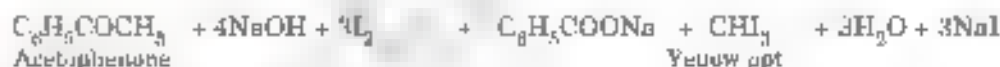
Benzaldehyde does not give ppt.

21. Benzaldehyde and Acetophenone

(i) Benzaldehyde forms silver mirror with ammoniacal silver nitrate solution (Tollen's reagent). Acetophenone does not react.



(ii) Acetophenone forms yellow ppt of iodoform with alkaline solution of iodine (iodoform test). Benzaldehyde does not react.

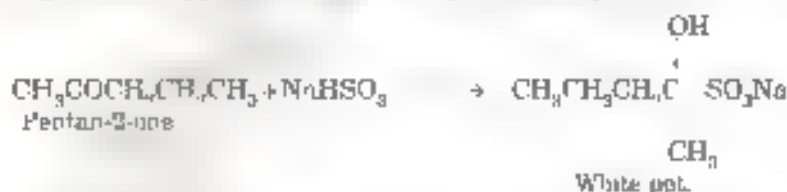


22. Pentan-3-one and Pentan-2-one

(i) Pentan-2-one forms yellow ppt with an alkaline solution of iodine (iodoform test) but pentan-3-one does not give iodoform test.



(ii) Pentan-2-one gives white ppt with sodium bisulphite while pentan-3-one does not.

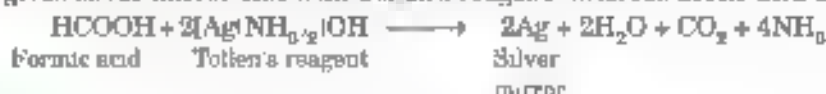


23. Acetophenone and Benzophenone Acetophenone gives yellow ppt with an alkaline solution of iodine (iodoform test). Benzophenone does not give this test.



24. Formic acid and Acetic acid

(i) Formic acid gives silver mirror test with Tollen's reagent whereas acetic acid does not give this test.



(ii) Formic acid gives white ppt with mercuric chloride solution.



Acetic acid does not give this test.

25. Acetic acid and Acetone

- i) Acetic acid reacts with NaHCO_3 to give effervescence due to evolution of CO_2 .



Acetone does not give effervescence with NaHCO_3 .

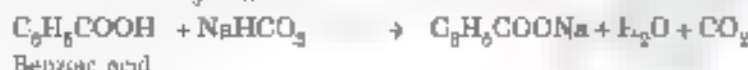
- ii) Acetone reacts with a. alkaline solution of iodine to give yellow ppt due to iodoform (iodoform test). Acetic acid does not give test.



- iii) Acetone also gives orange coloured ppt with 2,4-dinitrophenyl hydrazine, while acetic acid does not.

26. Phenol and Benzoic acid

- i) Benzoic acid reacts with NaHCO_3 to give effervescence due to the evolution of CO_2 .

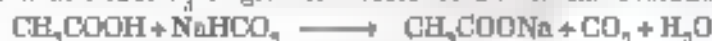


Phenol does not give effervescence.

- ii) Phenol gives violet colour with FeCl_3 solution but benzoic acid does not give such colour.

27. Phenol and Acetic acid

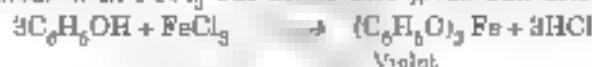
- i) Acetic acid reacts with NaHCO_3 to give effervescence due to the evolution of CO_2 .



Phenol does not give effervescence.



- ii) Phenol gives violet colour with FeCl_3 but acetic acid gives buff coloured ppt.

**28. Ethanol and Acetic acid**

- i) Acetic acid gives effervescence with NaHCO_3 due to the liberation of CO_2 .

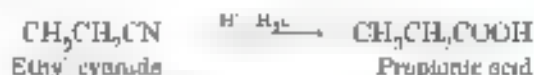


Ethanol does not give effervescence with NaHCO_3 .

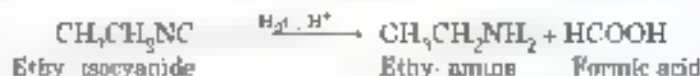
- ii) Ethanol gives yellow ppt with alkaline solution of I_2 (iodoform test) while acetic acid does not give this test.

**29. Ethyl cyanide and Ethyl isocyanide**

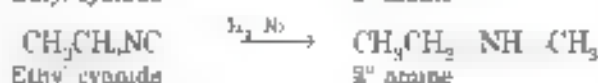
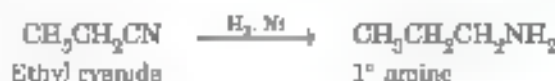
- i) Ethyl cyanide on hydrolysis with acids gives propionic acid.



On the other hand, ethyl isocyanide with dil. HCl gives ethyl amine and formic acid.



- ii) Ethyl cyanide on reduction with hydrogen in the presence of Ni or Pt gives primary amine while ethylisocyanide gives secondary amine.



A

P

P

E

N

D

I

C

E

S

30. Nitroethane and Ethylnitrite

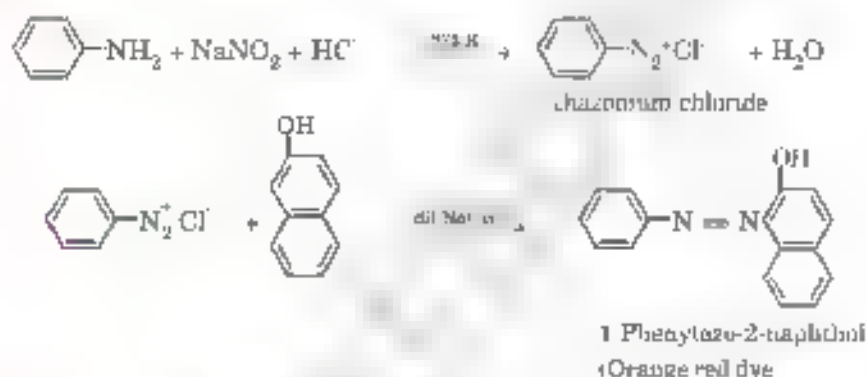
- Nitroethane on reduction with H_2/Ni gives primary amines while nitrite gives primary alcohol



- Ethylnitrite on hydrolysis form alcohol while nitroethane does not get hydrolysed



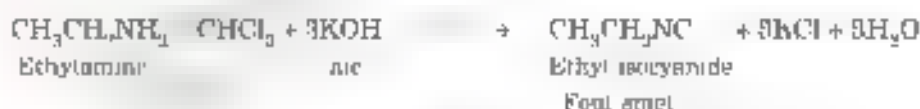
31. Ethylamine and Aniline Azo dye test. Dissolve the compound in conc HCl and add ice-cold solution of HNO_3 , $NaNO_2$ + dil HCl and then treat it with an alkaline solution of 2-naphthol. Appearance of brilliant orange or red dye indicates aniline



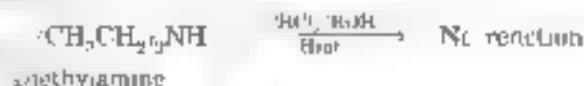
Ethylamine does not form dye. It will give brisk effervescence due to the evolution of N_2 but solution remains clear

32. Ethylamine and Diethylamine

- **Carbylamine test.** When heated with an alcoholic solution of KOH and $CHCl_3$, ethylamine gives foul smell of ethyl isocyanide



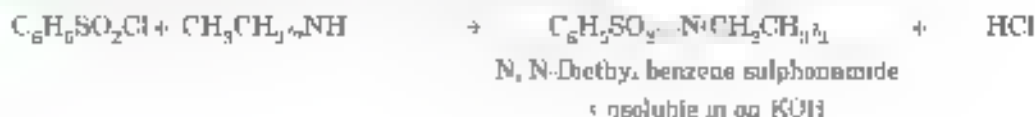
Diethylamine does not give the test.



- **Hinsberg's test.** When treated with Hinsberg's reagent benzene sulphonyl chloride $C_6H_5SO_2Cl$, ethylamine gives N-ethyl benzene sulphonamide which is soluble in aq. KOH solution



Diethylamine gives N,N-diethyl benzene sulphonamide which is insoluble in aqueous KOH



APPENDIX 4

Organic Conversions

● ORGANIC CONVERSIONS AND ROAD MAPS FOR ORGANIC CONVERSIONS

Organic conversions are very important part of study of organic chemistry. They provide very interesting interlink between different reactions and involve thorough understanding and skill to apply the reactions. Only practice and memory can induce confidence for attempting the conversions. Some basic road maps or memory aids are given in this appendix.

Basic tips

- On your paper reagents must be listed in different reactions. These are separate reactions and be drawn

ALIPHATIC CONVERSIONS

The conversions may be divided into three types

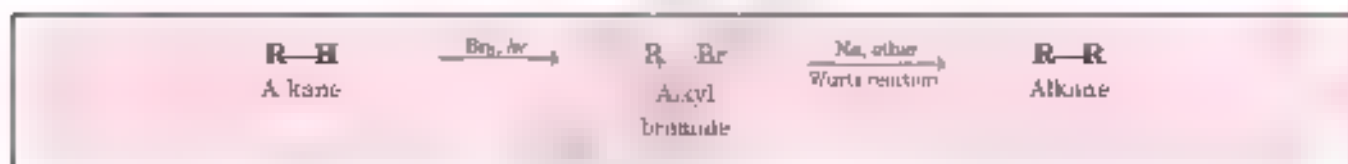
1 Ascent of series. These involve the conversion of an organic compound into next higher homologues. Therefore, carbon atom is introduced in the chain.

2. Descent of series. There involves the conversion of an organic compound into its next lower homologue. Therefore, a carbon atom is removed from the chain.

3. **Simple conversions.** These involve general conversions, such as, the turning of compounds to another

1 Conversions based on ascent series

(g) **By Wurtz reaction.** These involve conversion from lower hydrocarbon to higher hydrocarbon



For example,

(d) Methane to ethane



(ii) Ethane to butane



But, if we wish to prepare propane from ethane, the reaction is

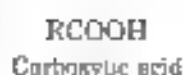


However this is not a good method because in addition to propane, ethane and butane will also be formed by the reaction of ethyl chloride and methyl chloride.

(b) **Through cyanide.** This is an important method for ascending the series. The basic reaction in these conversions is



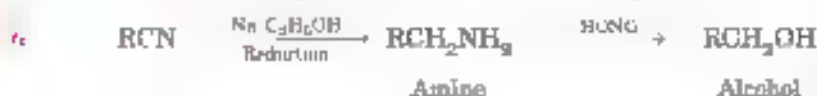
The alkyl cyanide has one carbon atom more than the alkyl halides. This can be directly converted into other compounds through certain steps.



Foot cal. salt
with cal. foripate

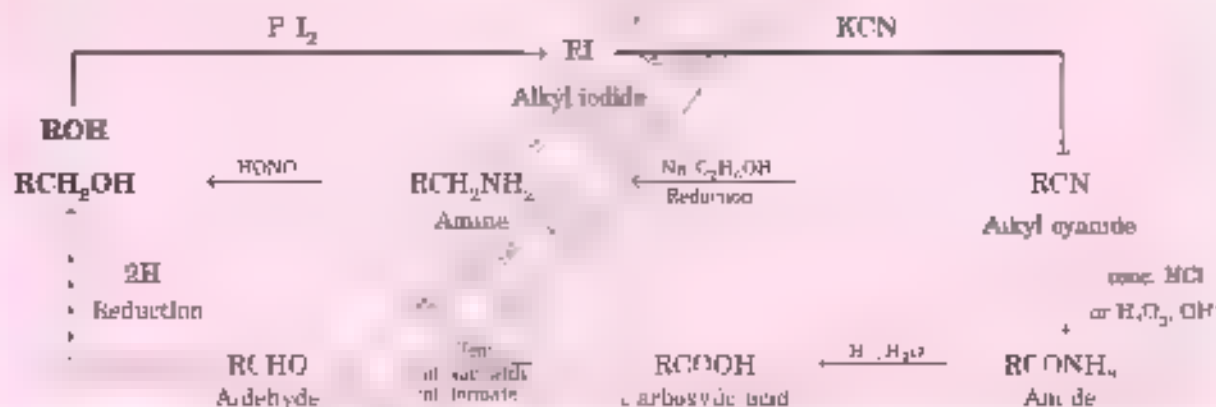


If calcium salt of carboxylic acid is heated alone, it gives ketone



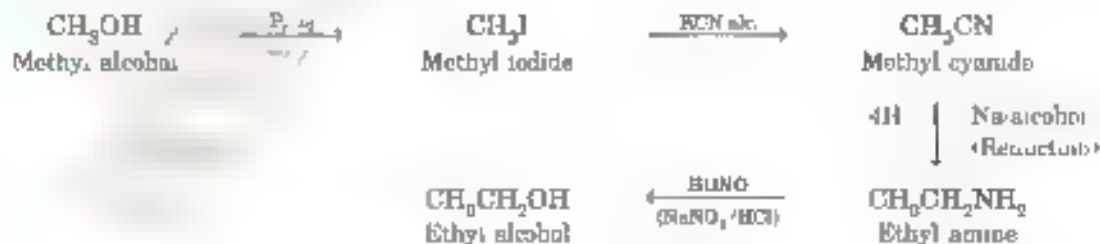
Amide can be converted to carboxylic acid and so on.

These reactions may be summarized as

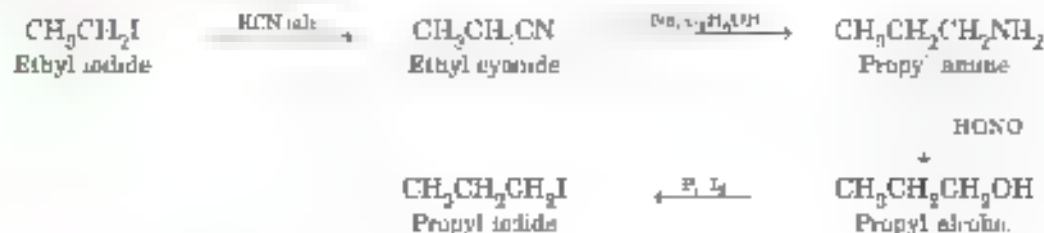


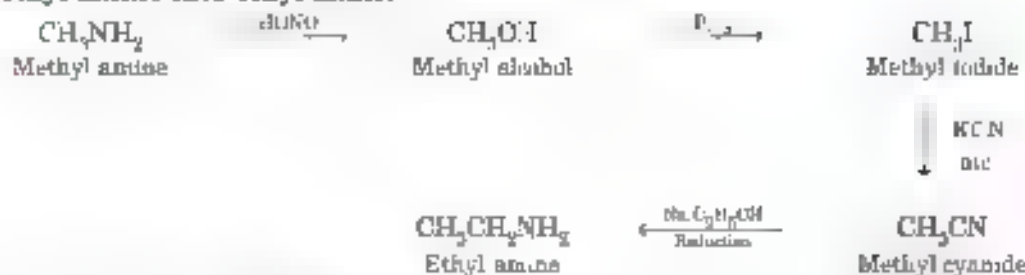
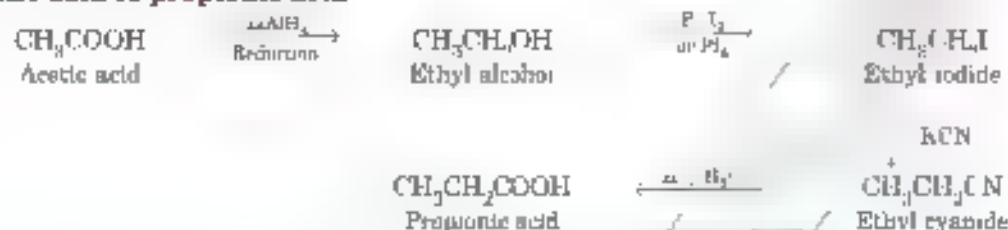
For example

(f) Methyl alcohol to ethyl alcohol

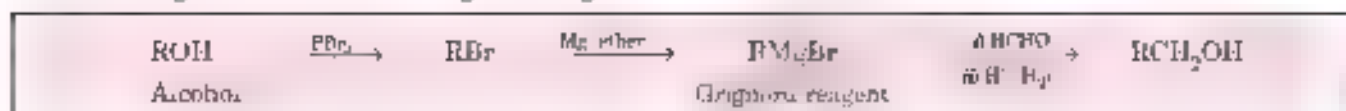


(27) Ethyl iodide to propyl iodide



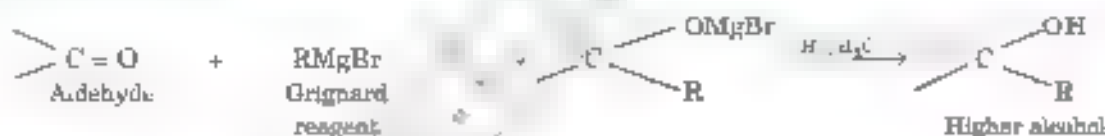
(iii) Methyl amine into ethyl amine**(iv) Acetic acid to propionic acid**

(v) Through Grignard reagent. This route is followed for converting lower alcohol, ROH to a higher alcohol through the formation of Grignard reagent.

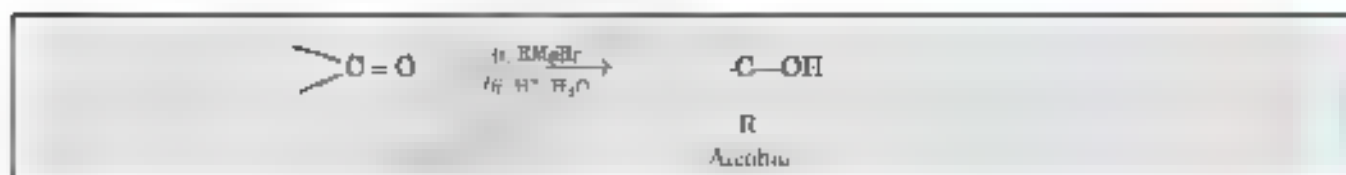


By using different aldehydes or Grignard reagents, different products can be obtained.

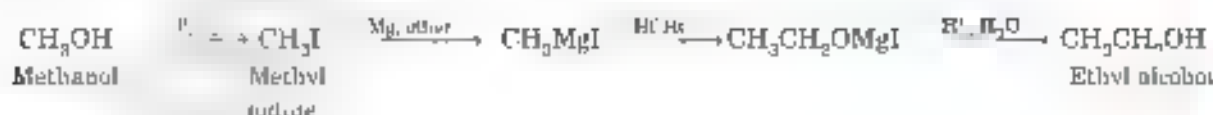
The main reaction in these is the reaction of an aldehyde with a Grignard reagent followed by hydrolysis to give alcohols.

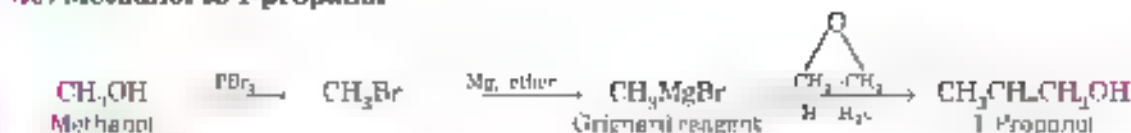
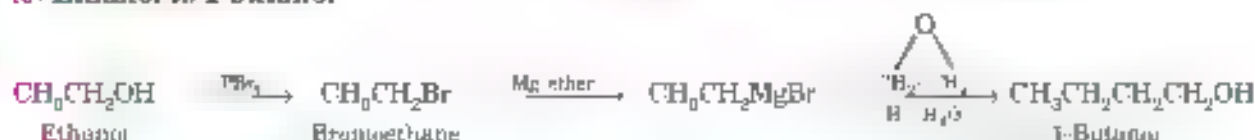


The reaction may be written as

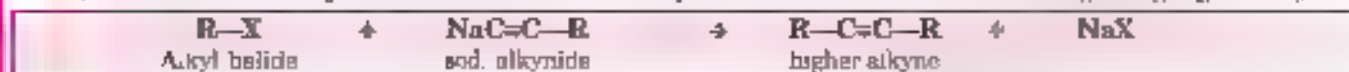


For example,

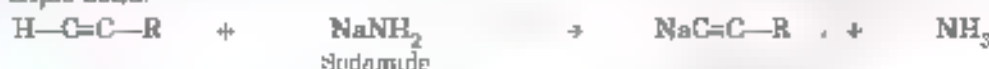
(i) Methanol to ethanol**(ii) Methanol to Propan-2-ol****(iii) Methanol to ethanol**

(c) Methanol to 1-propanol**(c) Ethanol to 1-butanol**

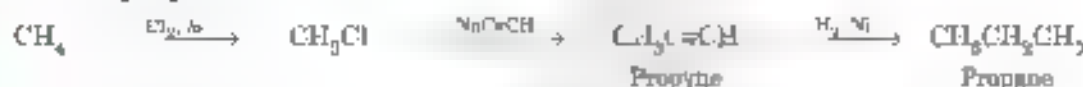
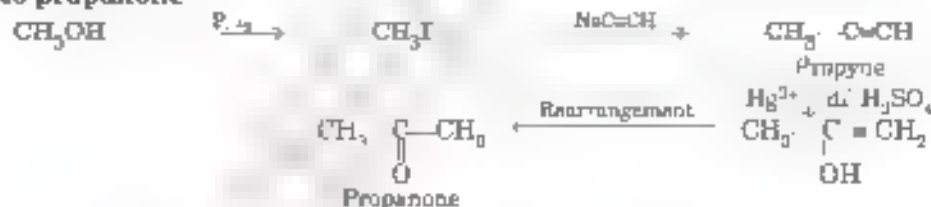
(d) Reaction of alkyl halides with sodium alkynides. This route is followed for getting higher alkynes



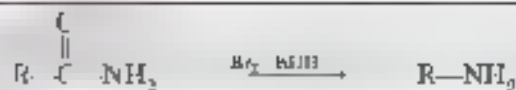
Sodium alkynides needed for the above purpose are formed by the reaction of sodamide with alkynes containing triple bond.



For example,

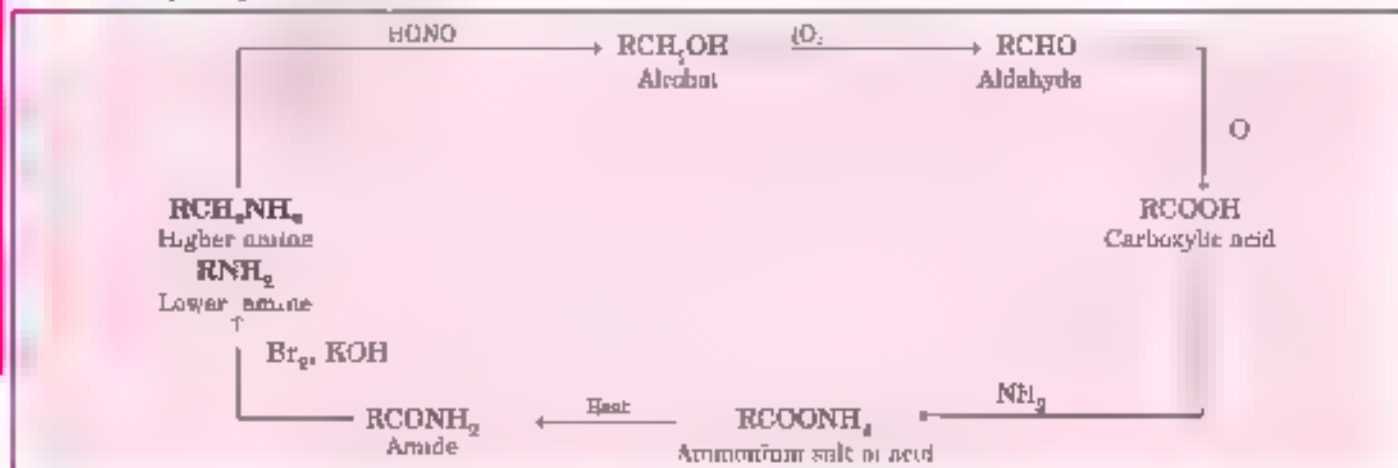
(i) Methane to propane**(ii) Acetylene to but-1-yne****(iii) Methanol to propanone****2. Conversions based on descent series**

(a) Through Hoffmann's bromamide reaction. The basic reaction in these conversions is known as Hoffmann's bromamide reaction:



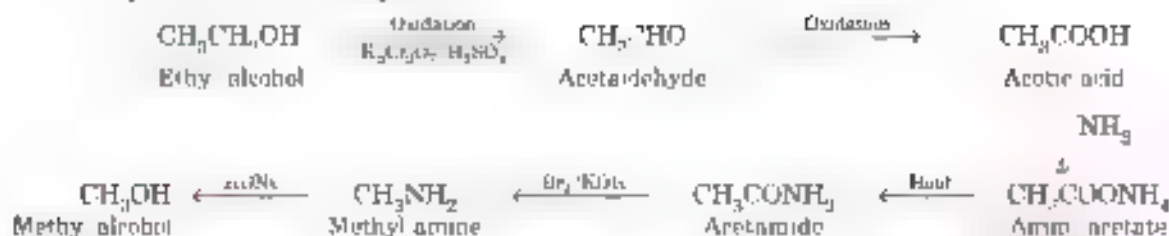
The amine formed has one carbon atom less than the parent amide

The steps may be shown as:

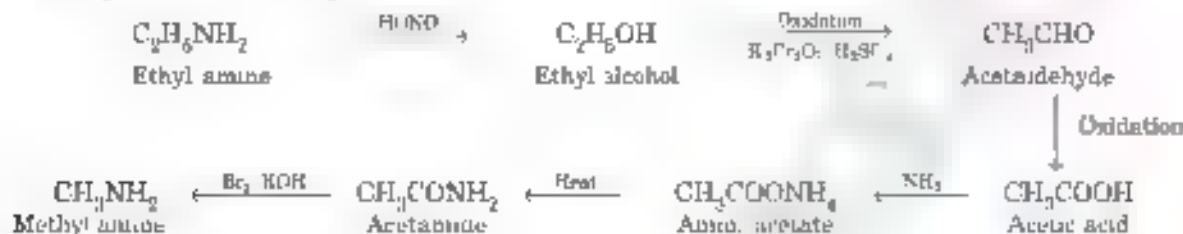


For example,

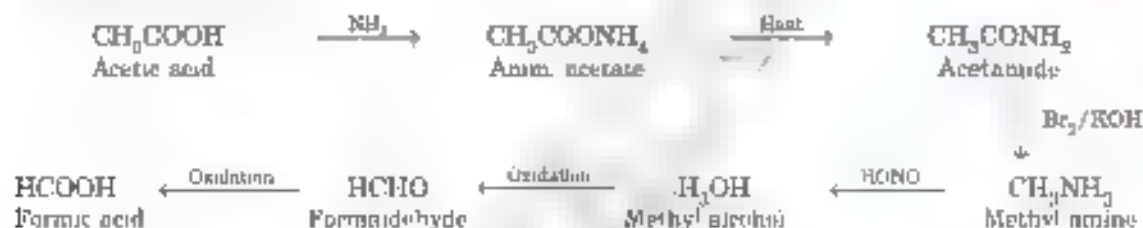
(i) Ethyl alcohol to methyl alcohol



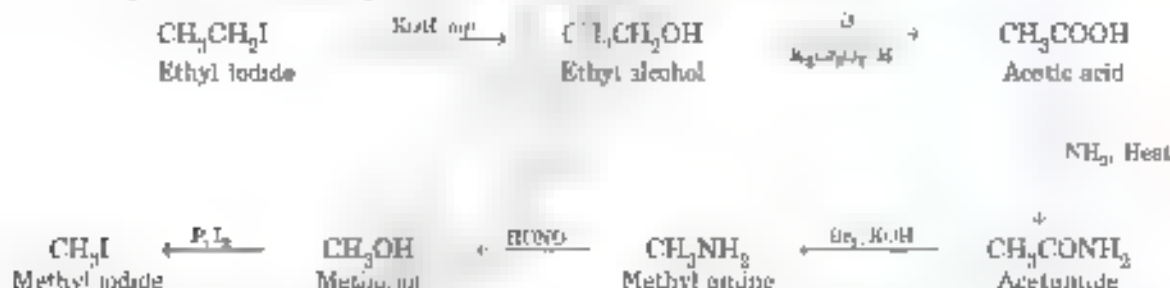
(ii) Ethylamine to methylamine



(iii) Acetic acid to formic acid



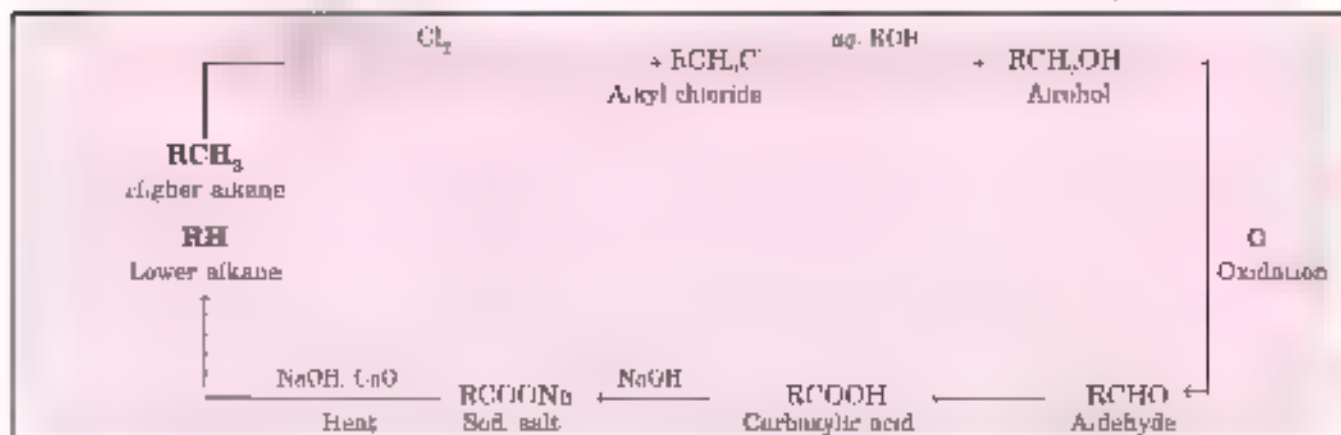
(iv) Ethyl iodide to methyl iodide



(b) Through decarboxylation of a fatty acid with sodalime $\text{NaOH} + \text{CaO}$ The basic reaction in these conversions is



The hydrocarbon obtained has one C-atom less than the acid. The different steps may be shown as

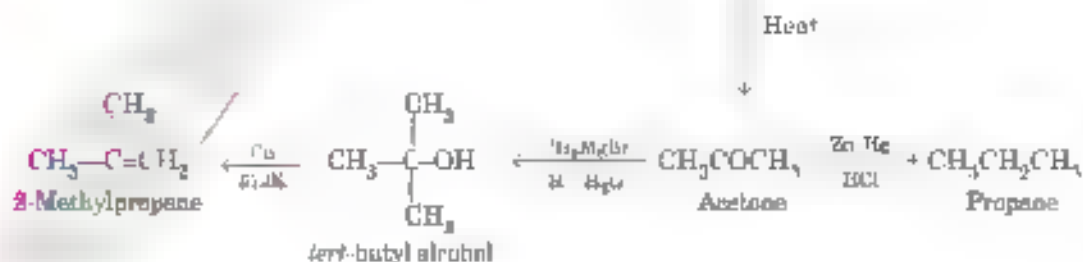


• Propionic acid to ethane

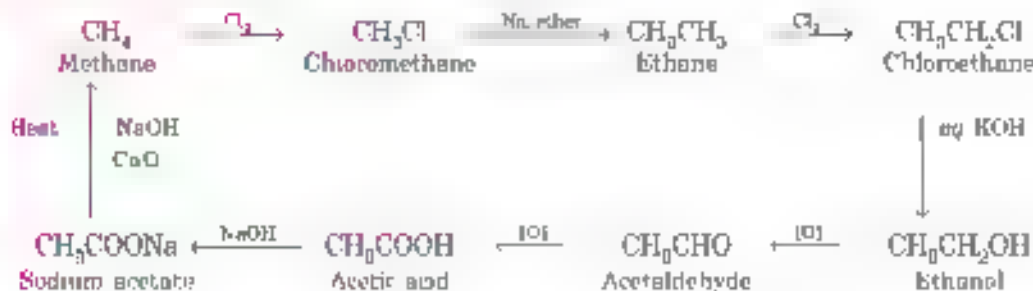


Some common road maps involving different conversions are given below:

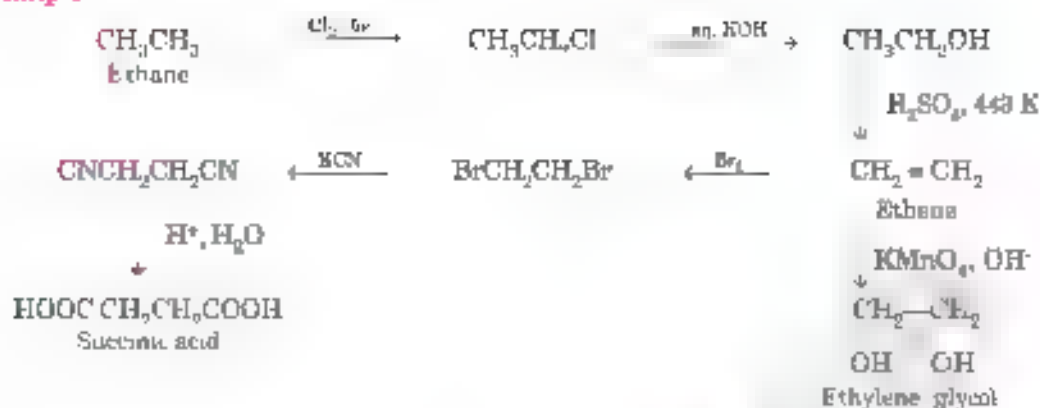
Road map 1



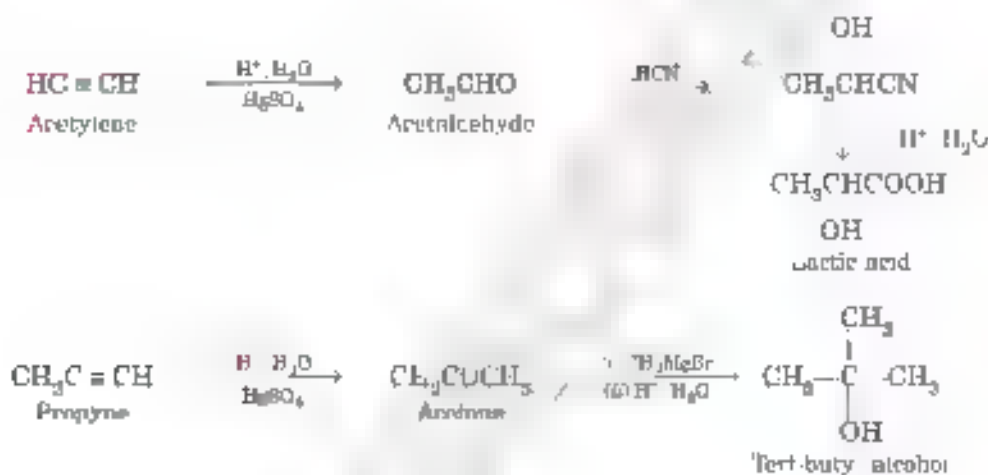
Road map 4



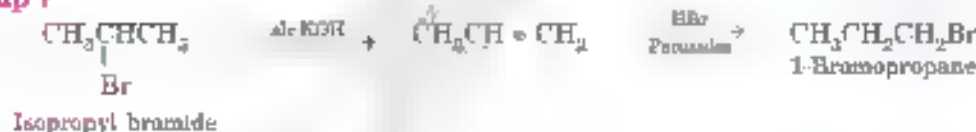
Road map 5



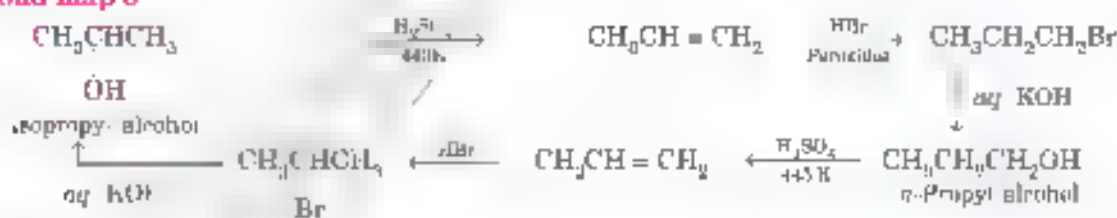
Road map 6



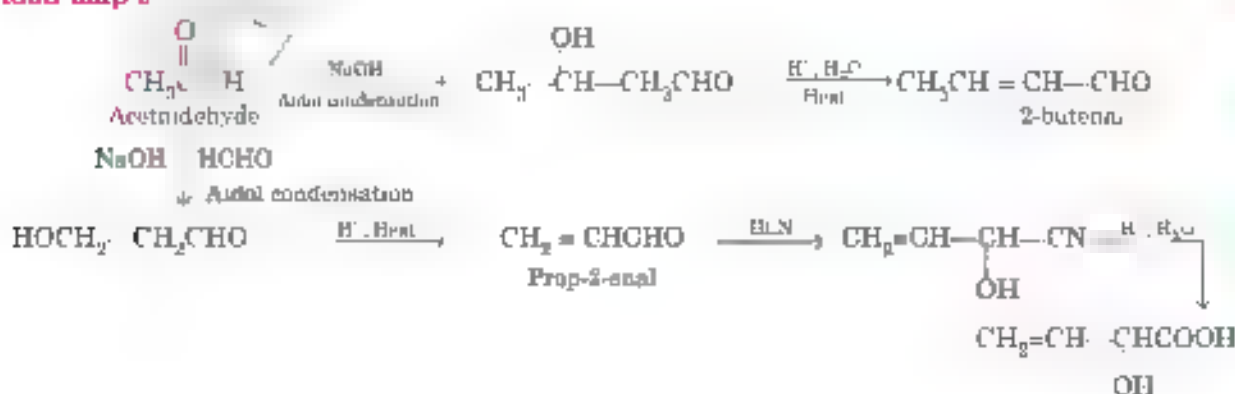
Road map 7



Road map 8

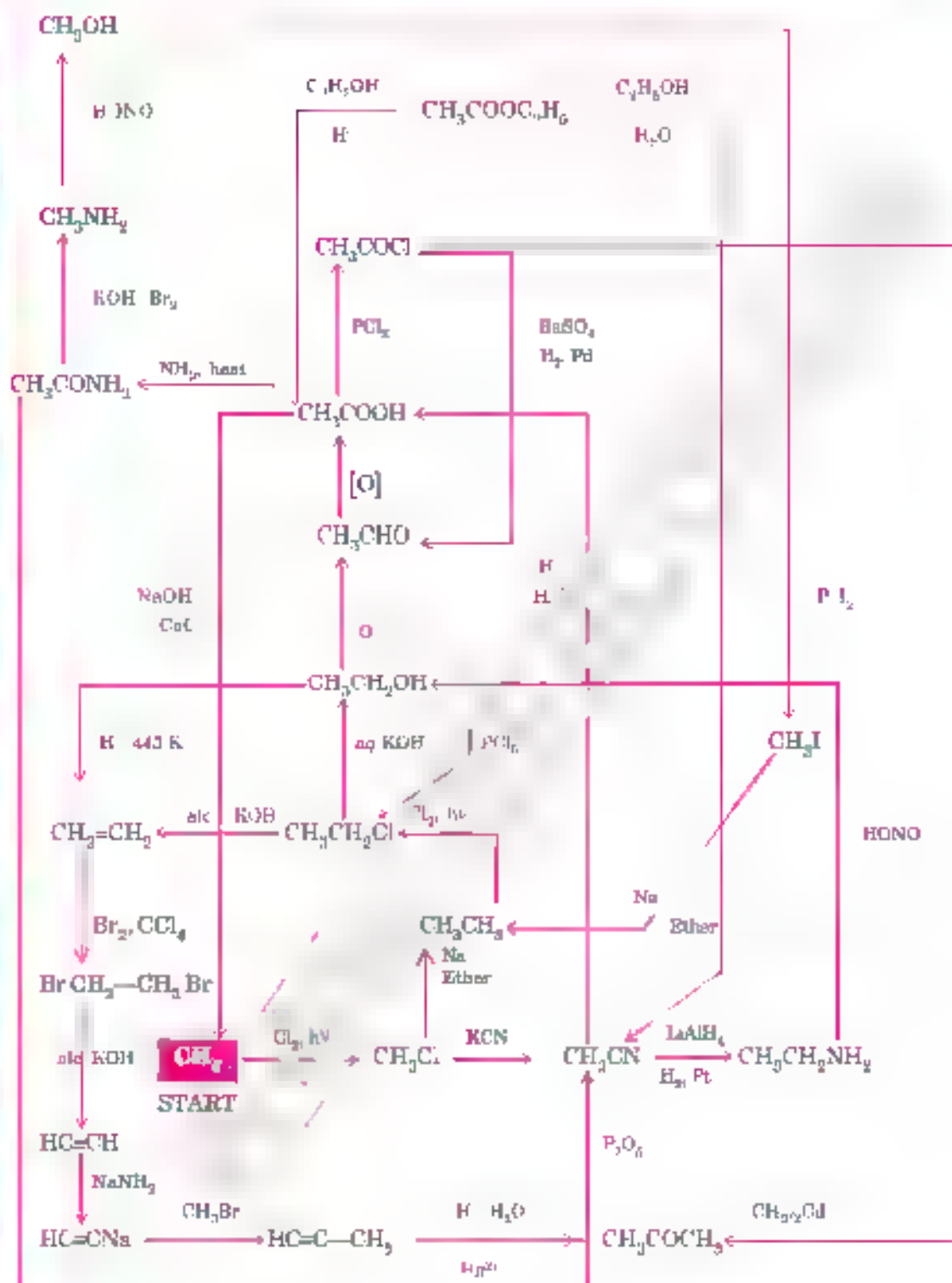


Road map 9



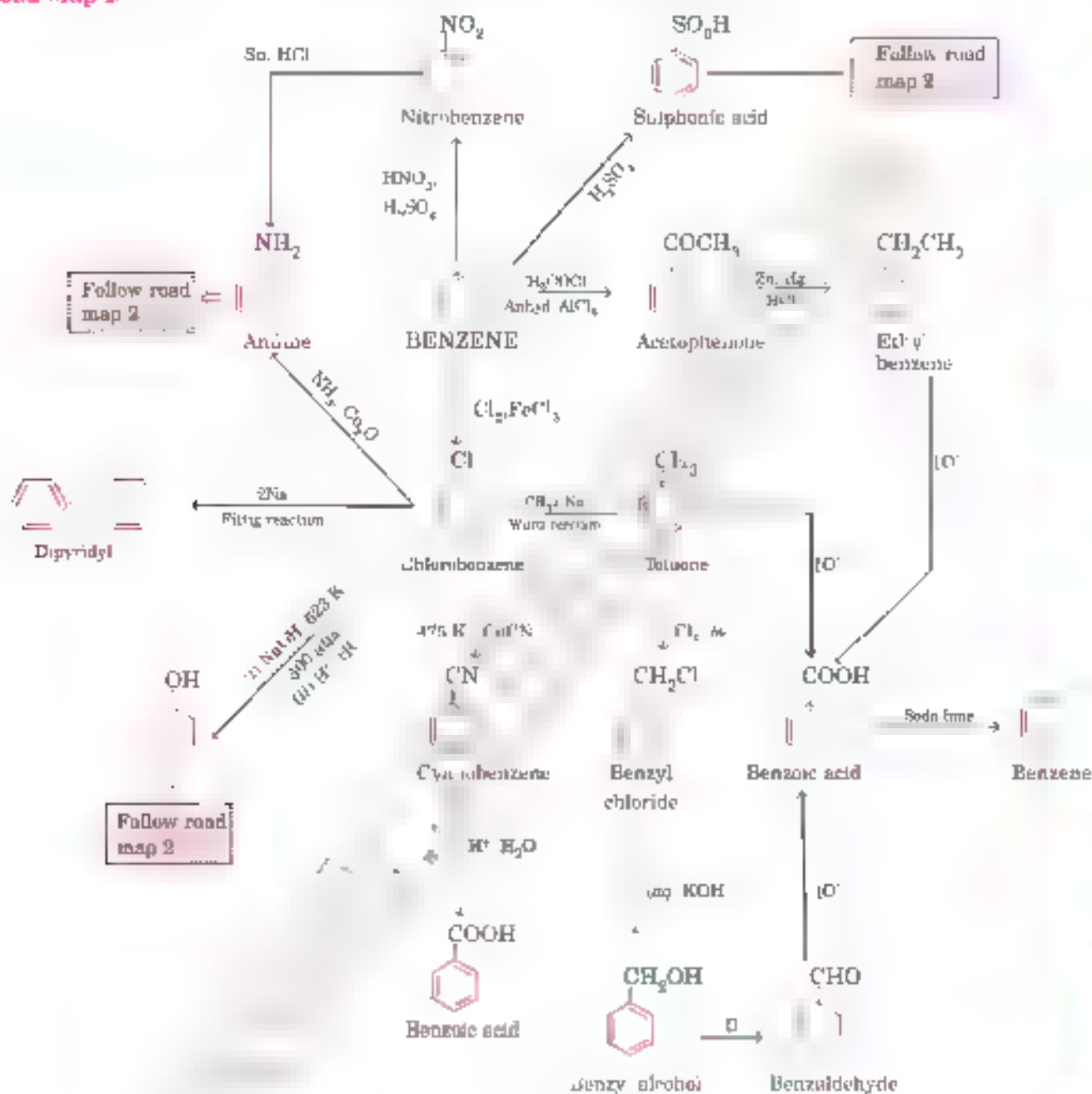
Summary of Routes

ATLAS OF BASIC ORGANIC CONVERSIONS Aromatic

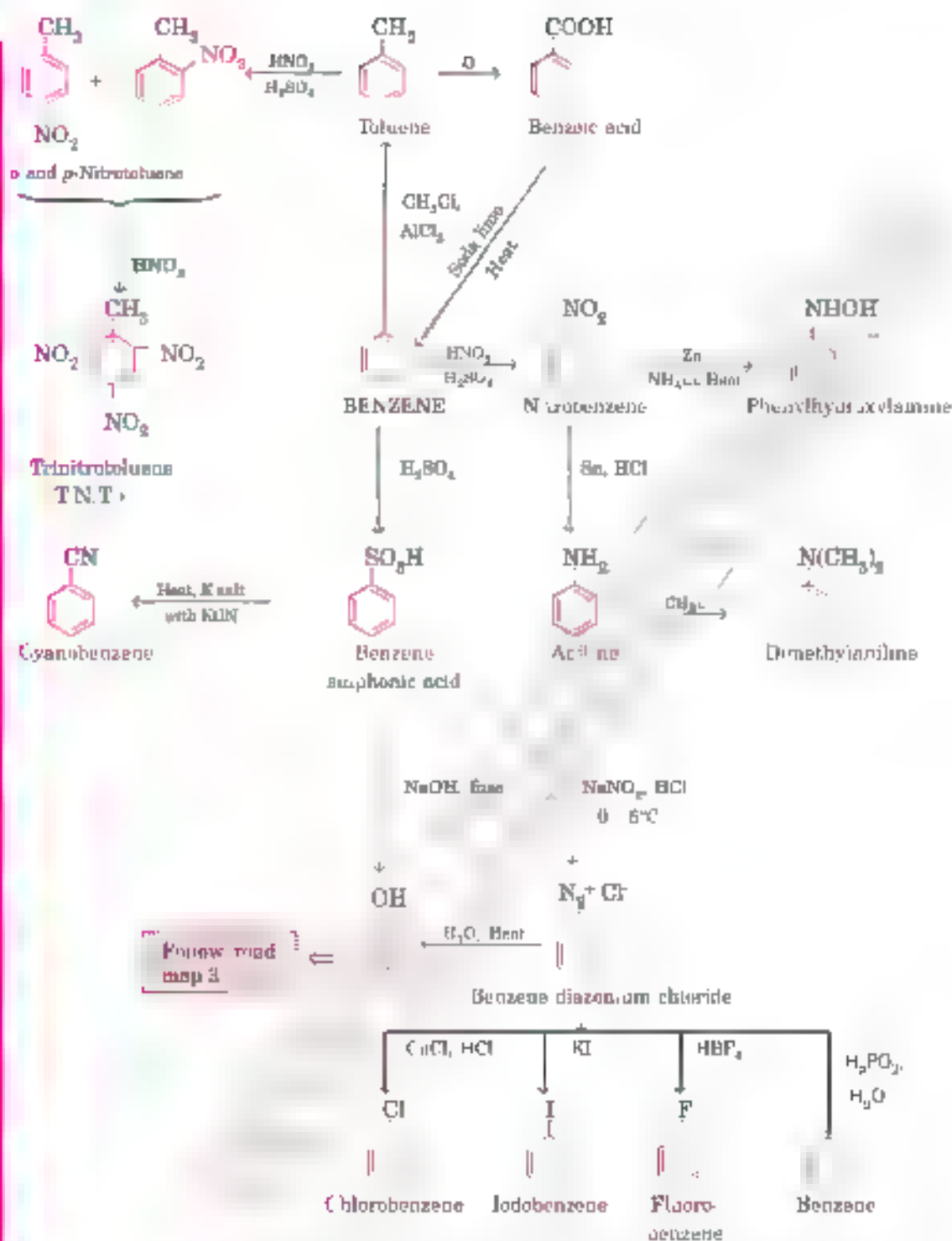


AROMATIC CONVERSIONS

These are based upon the general reactions of different substances. Some common road maps are Road Map 1.

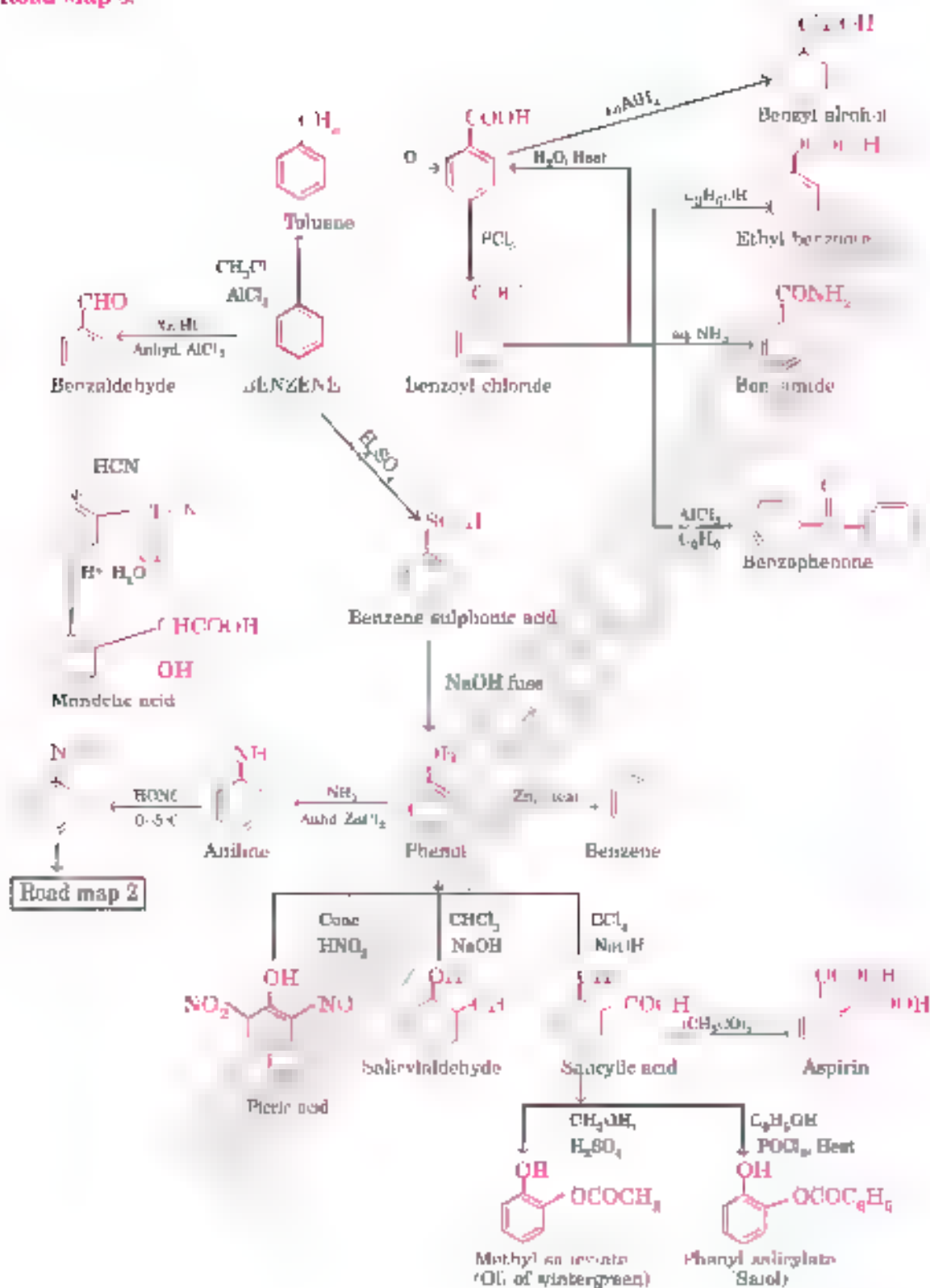


Road Map 2



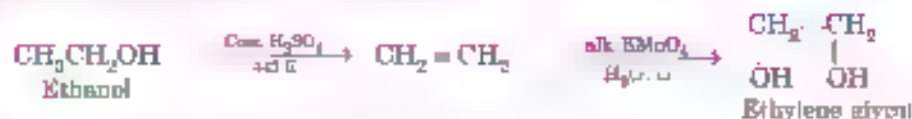
The different examples are already discussed in Chapters 8, 9 and 10

Road Map 3.

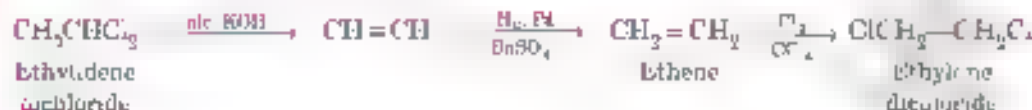


SOME TYPICAL CONVERSIONS

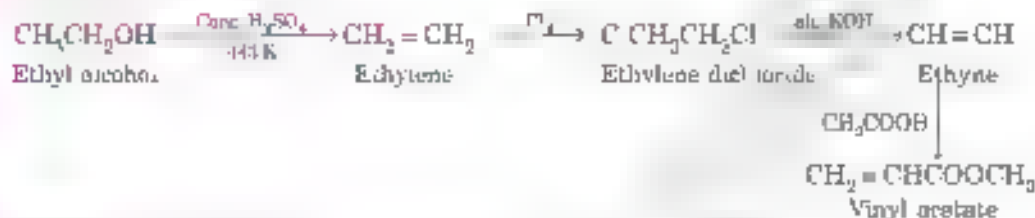
1. Ethanol to ethanedial (ethylene glycol)



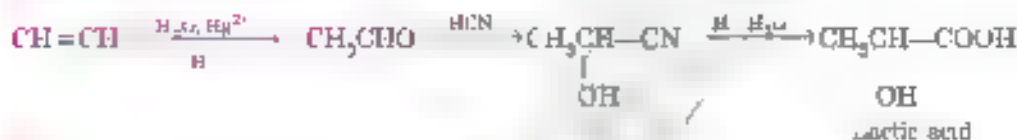
2. Ethyldiene dichloride to ethylene dichloride



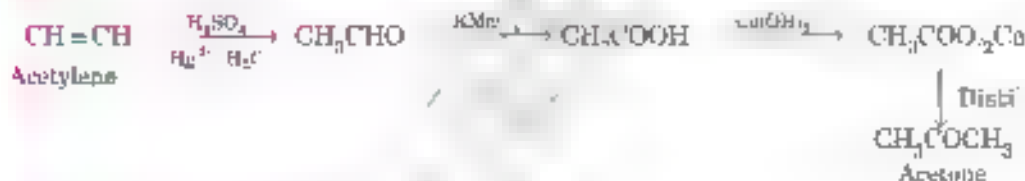
3. Ethyl alcohol to vinyl acetate



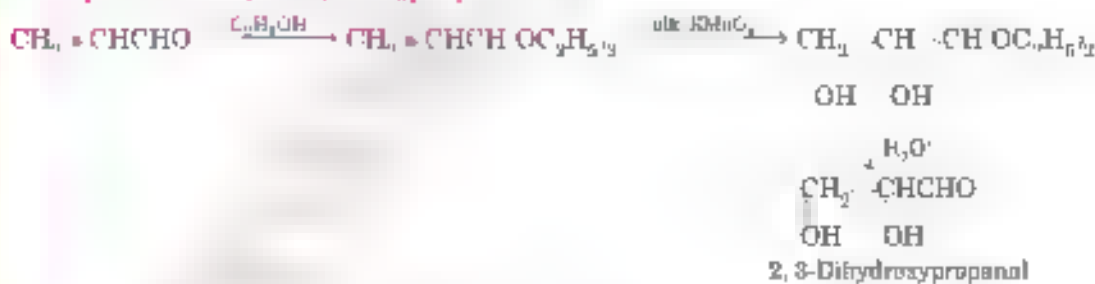
4. Acetylene to lactic acid



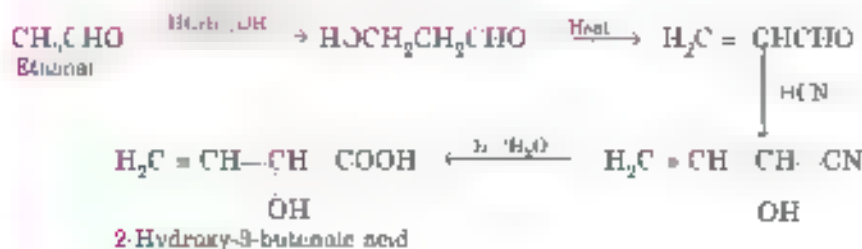
5. Acetylene to acetone



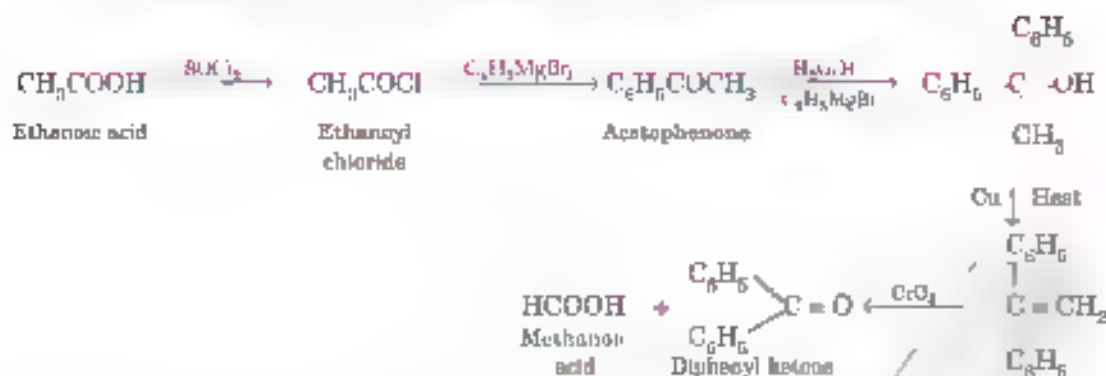
6. Prop-2-enal to 2,3-dihydroxypropanal



7. Ethanal to 2-hydroxy-3-butenal acid



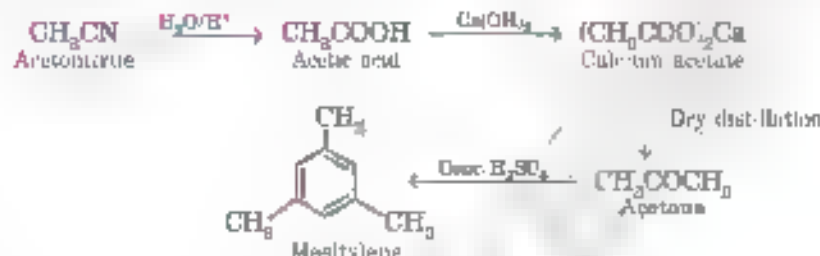
8. Ethanoic acid to a mixture of methanoic acid and diphenyl ketone



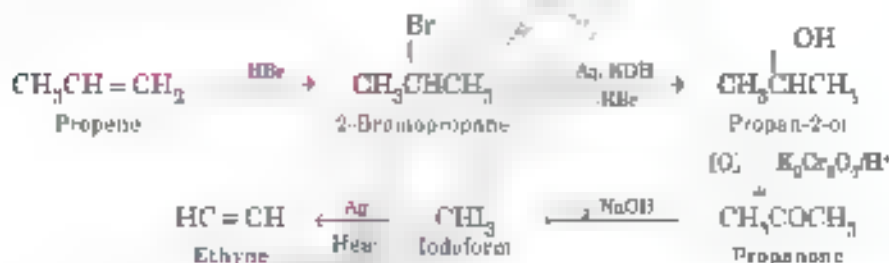
9. n-Propyl alcohol to isopropyl alcohol



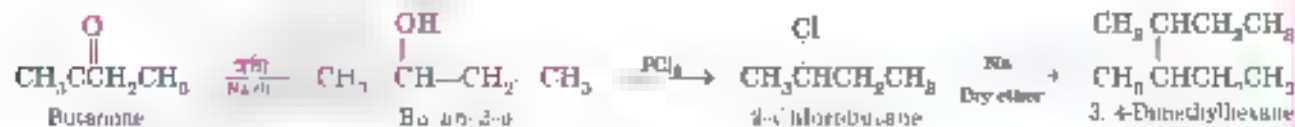
10. Acetonitrile to mentylene



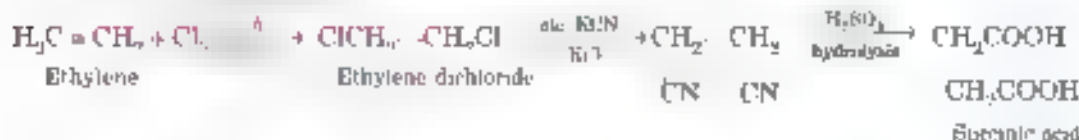
11. Propene to ethyne



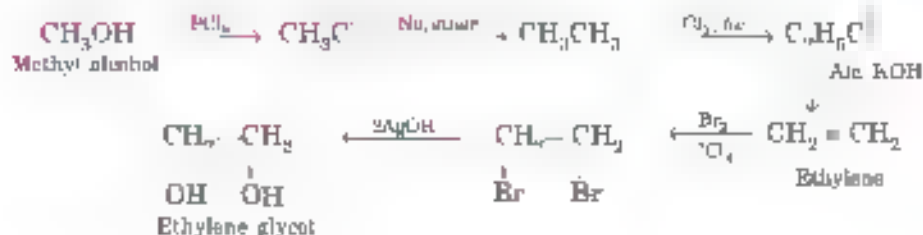
12. Butanone to 3,4-dimethylhexane

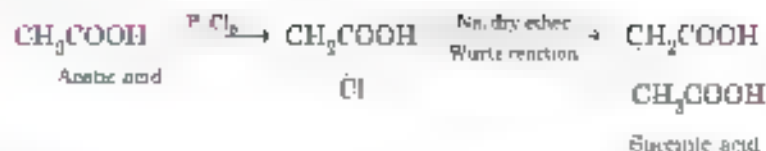
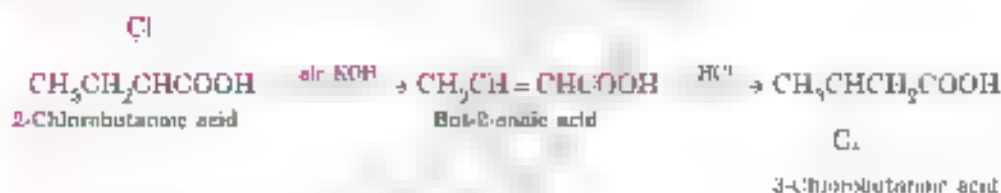
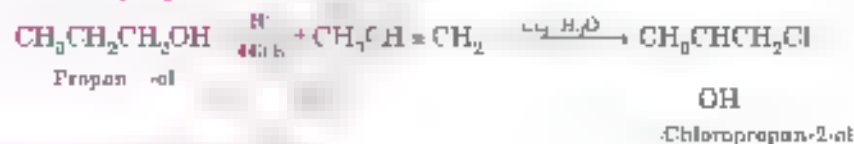
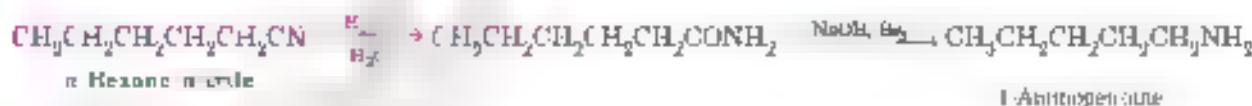
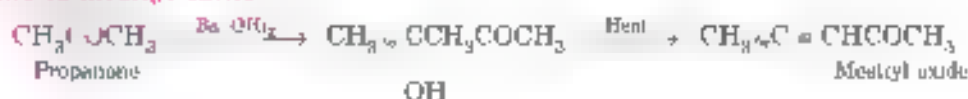
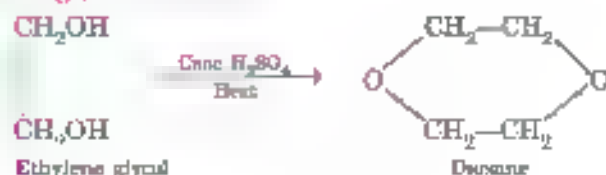


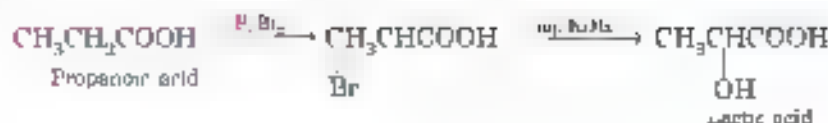
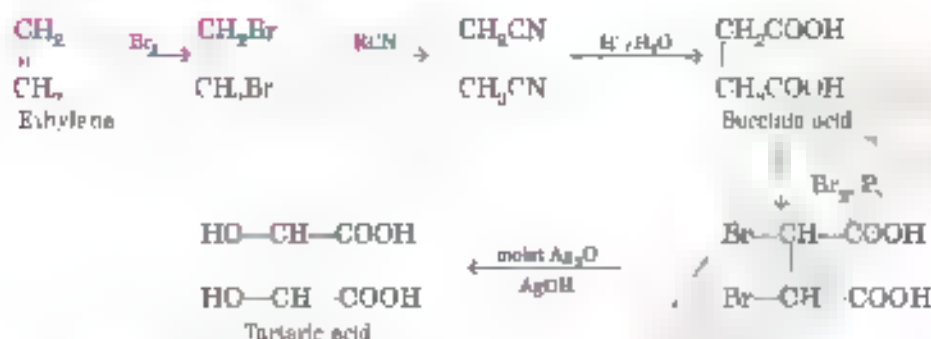
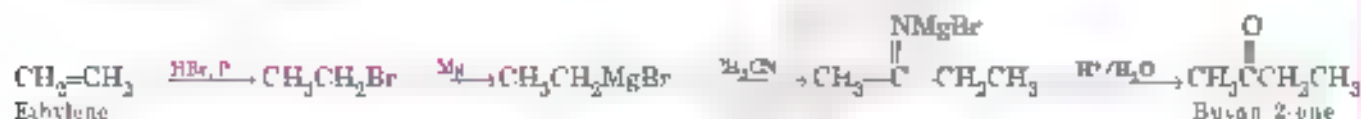
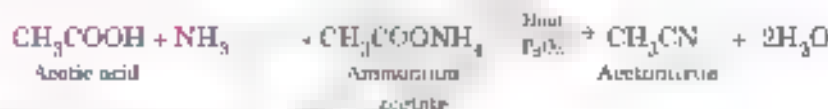
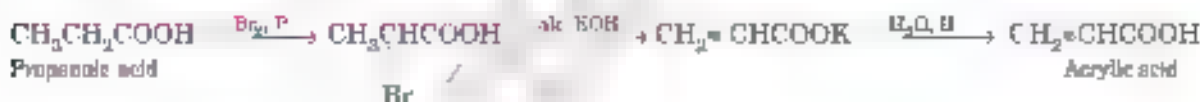
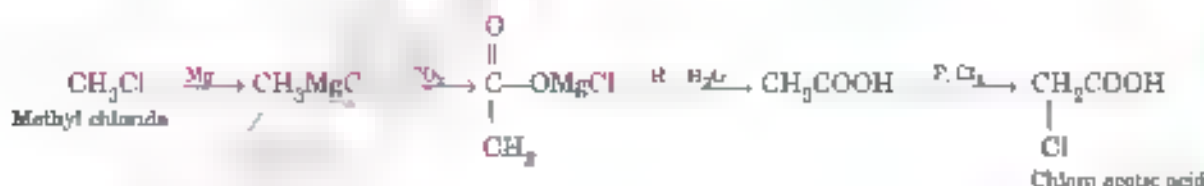
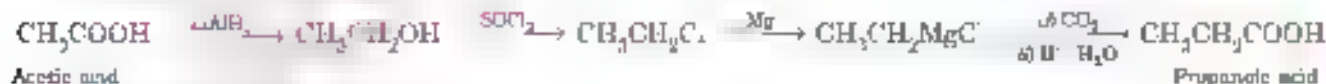
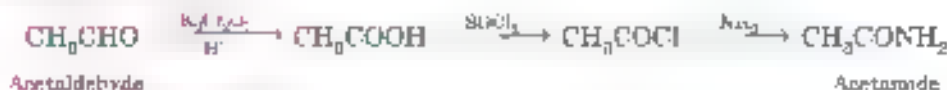
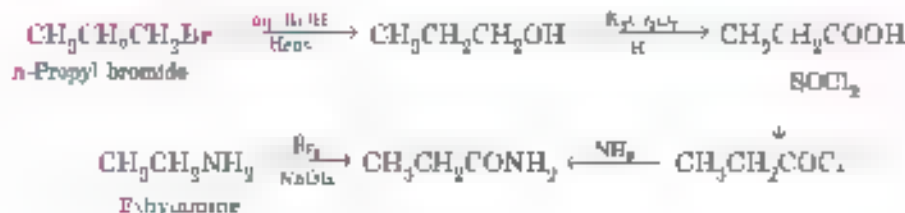
13. Ethylene to succinic acid

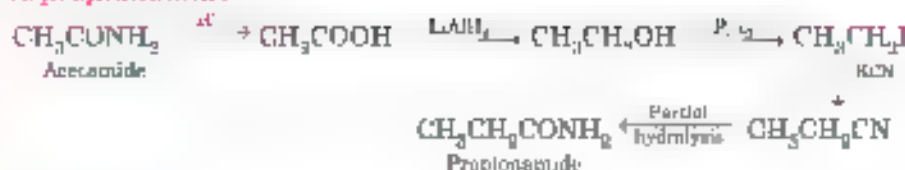
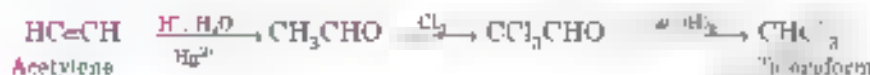
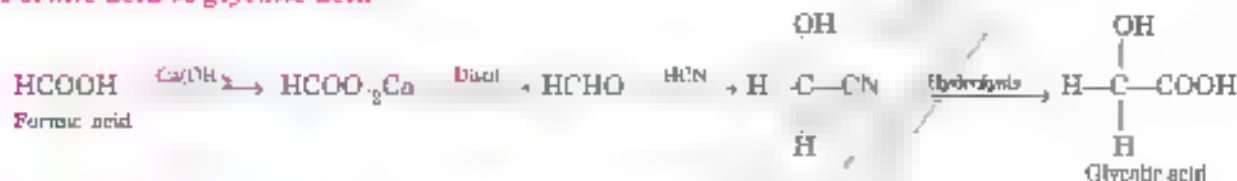
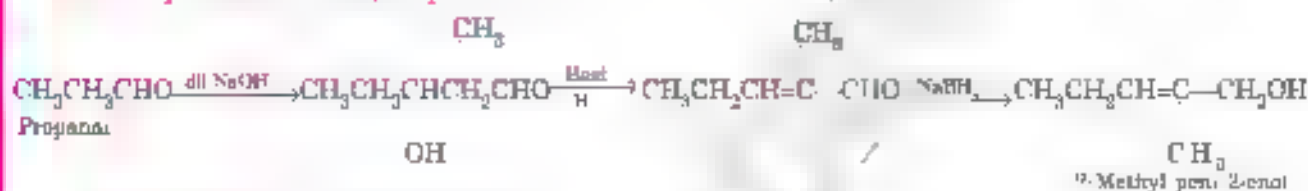
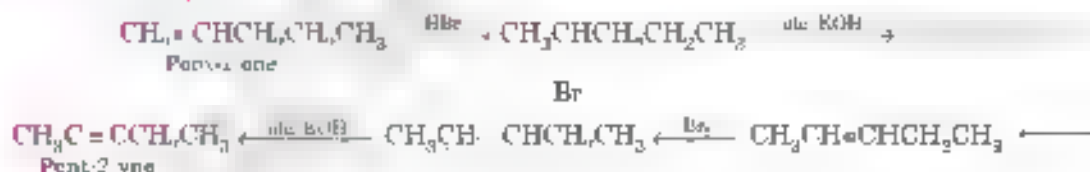
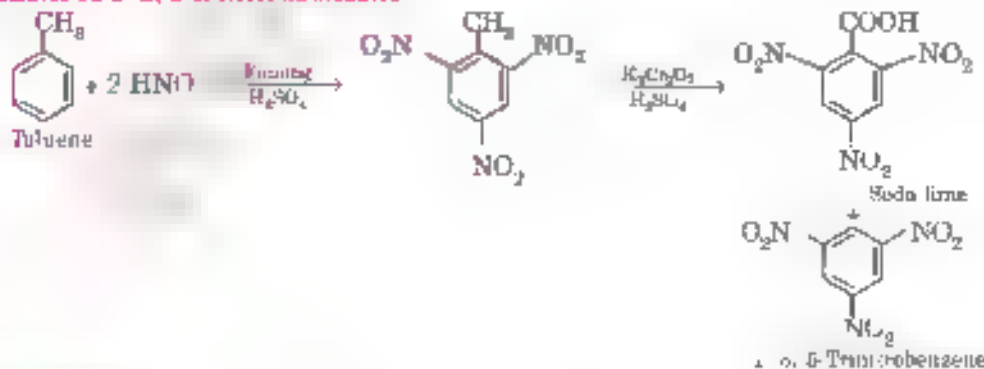
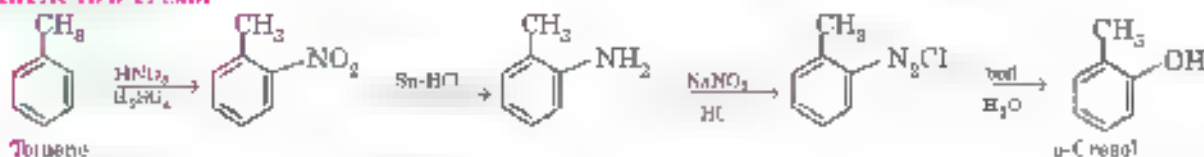


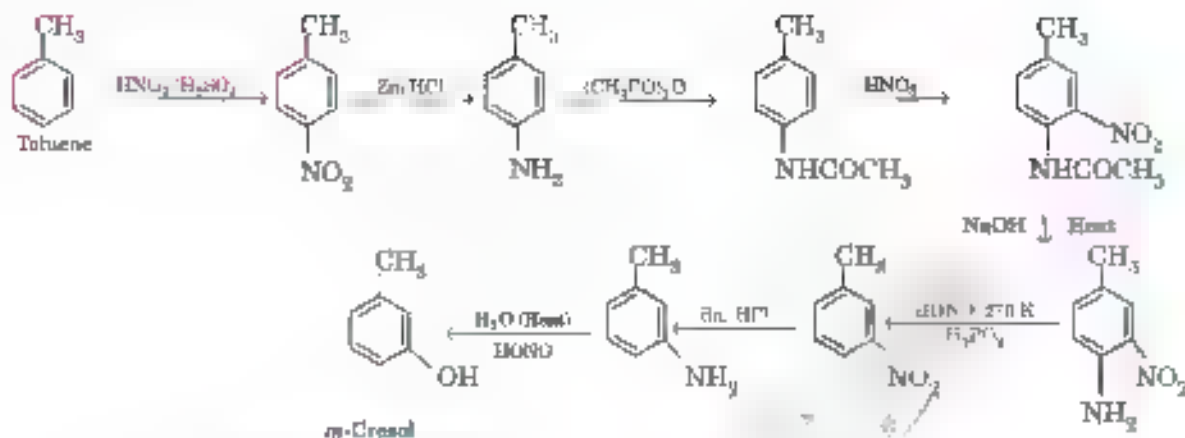
14. Methyl alcohol to ethylene glycol



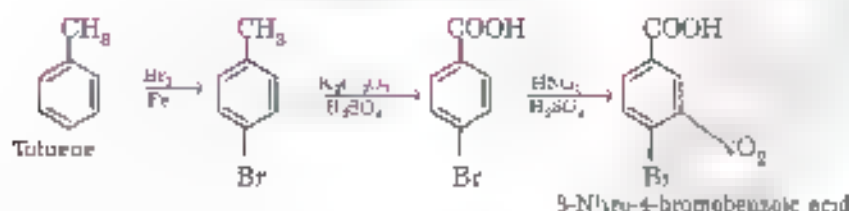
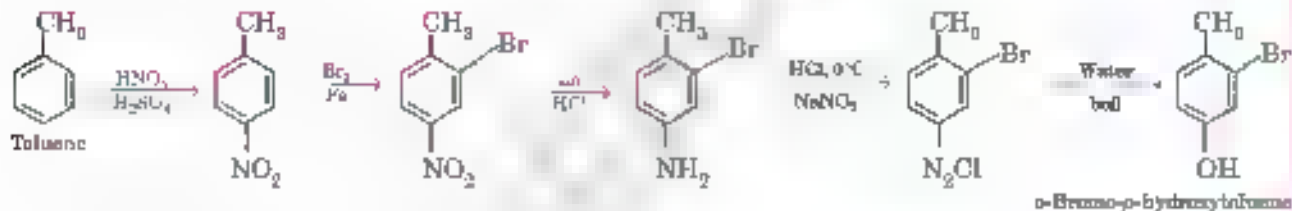
15. Acetic acid to succinic acid**16. Acetic acid to glycine****17. Acetic acid to acetaldehyde****18. Propanoic acid to Propan-2-ol****19. 2-Chlorobutanoic acid to 3-chlorobutanoic acid****20. Propan-1-ol to 1-chloro-propan-2-ol****21. n-Hexane nitrile to 1-amino-propane****22. Acetaldehyde to malonic acid****23. Propanone to methyl oxide****24. Ethylene glycol to dioxane**

25. Propanoic acid to lactic acid**26. Ethylene to tartaric acid****27. Ethylene to butan-2-one****28. Acetic acid to acetonitrile****29. Propanoic acid to acrylic acid****30. Methyl chloride to chloroacetic acid****31. Acetic acid to propanoic acid****32. Acetaldehyde to acetamide****33. n-Propyl bromide to ethylamine**

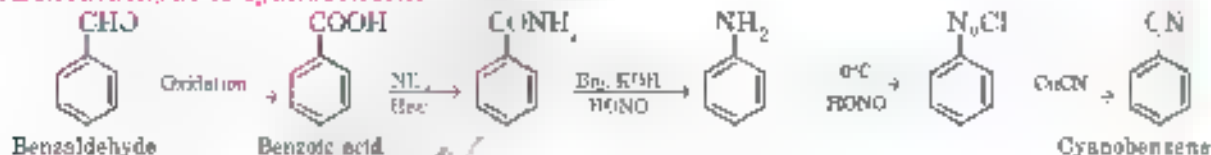
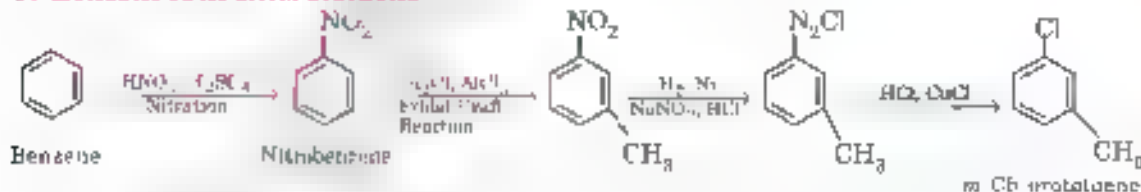
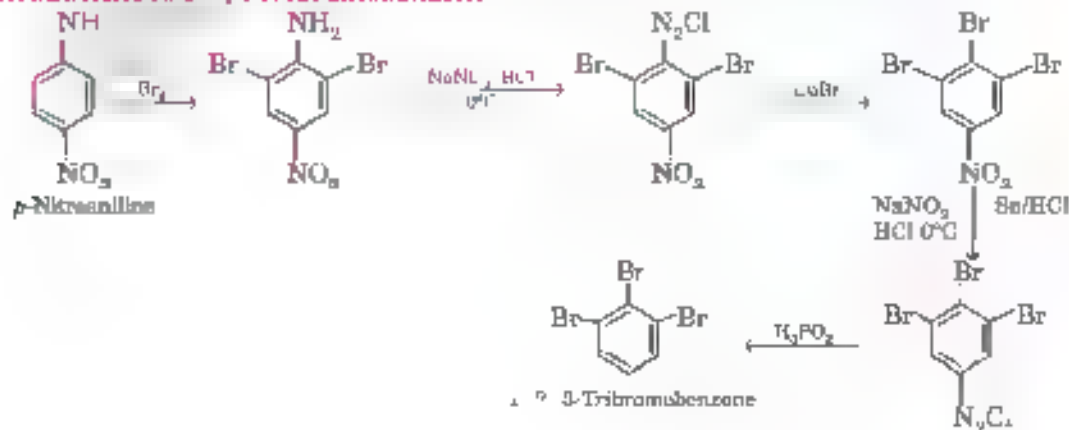
34. Acetamide to propionamide**35. Acetylene to chloroform****36. Formic acid to glycolic acid****37. Propanal to 3-methyl-3-pentanol****38. Acetaldehyde to acetoacetic ester****39. $\text{CH}_3\text{CH}_2\text{C}\equiv\text{CH}$ to $\text{CH}_3\text{CH}_2\text{CH}_2\text{COCH}_3$ three steps,****40. Pent-1-ene to Pent-2-yne****41. Toluene to 1,3,5-trinitrobenzene****42. Toluene to o-cresol**

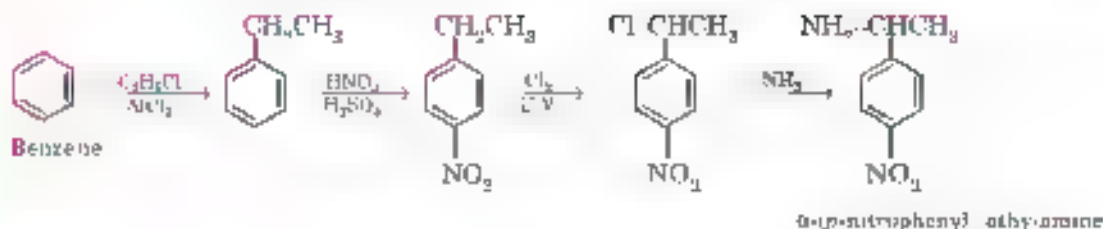
43. Toluene to *m*-cresol

44. Toluene to 3-nitro-4-bromobenzoic acid

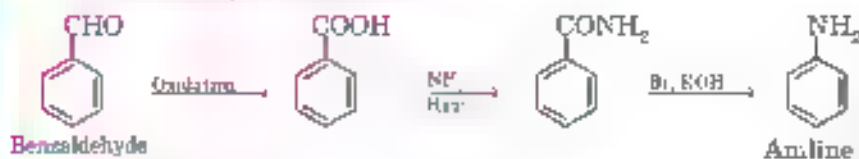
45. Toluene to *o*-bromo-*p*-hydroxytoluene

46. Benzaldehyde to cyanobenzene

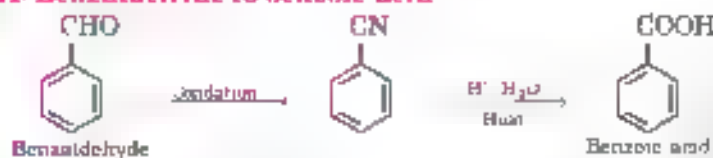
47. Benzene to *m*-chlorotoluene48. *p*-Nitroaniline to 1,2,3-tribromobenzene

49. Benzene to α -(p-nitrophenyl) ethylamine

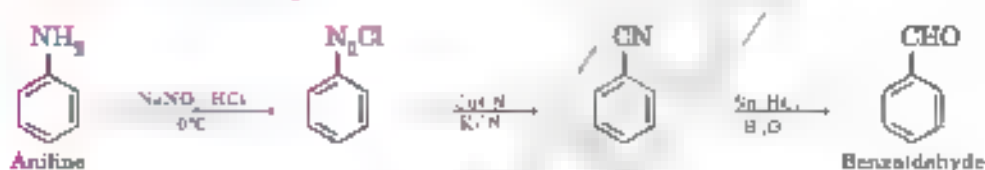
50. Benzaldehyde to aniline



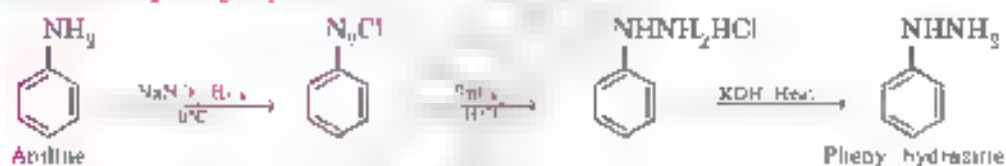
51. Benzaldehyde to benzoic acid



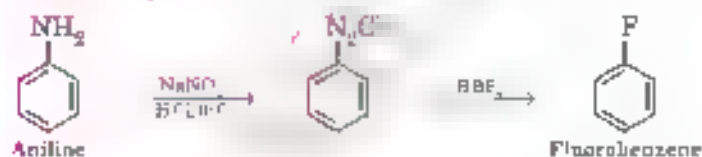
52. Aniline to benzaldehyde



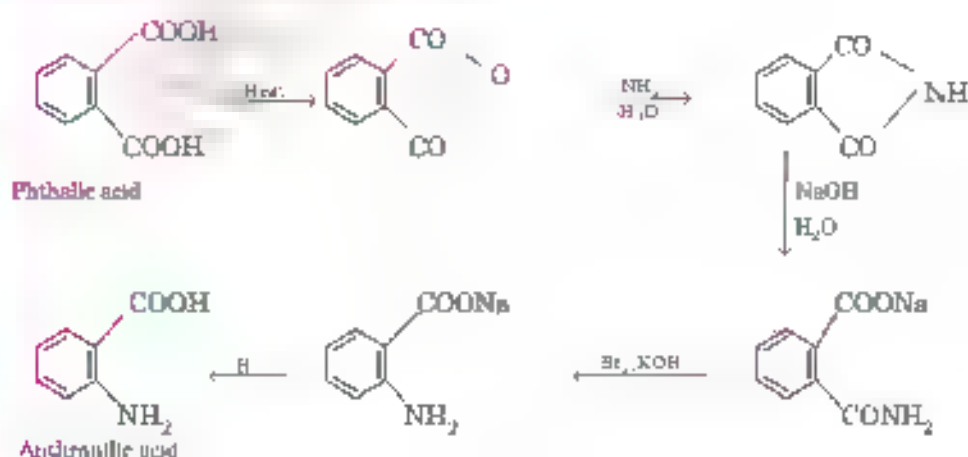
53. Aniline to phenyl hydrazine

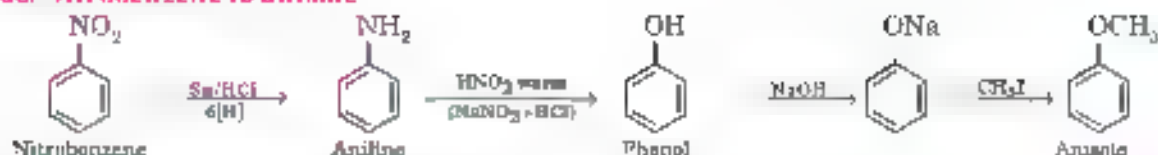
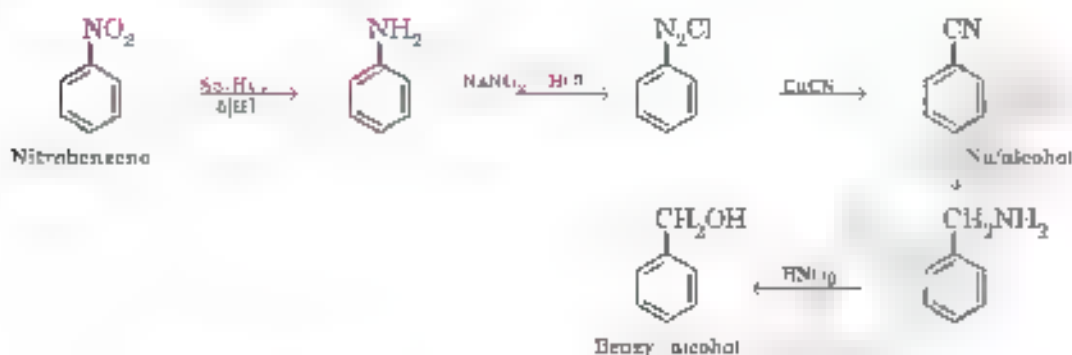
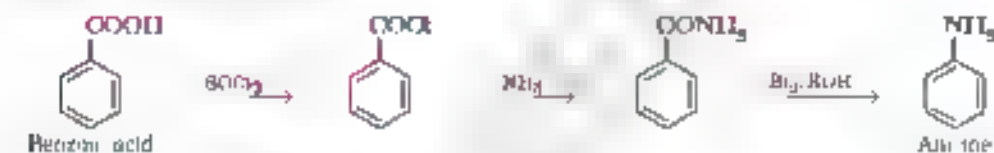
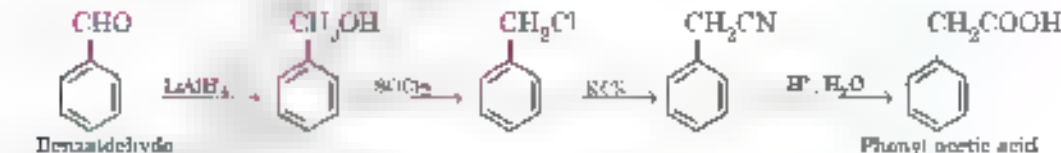
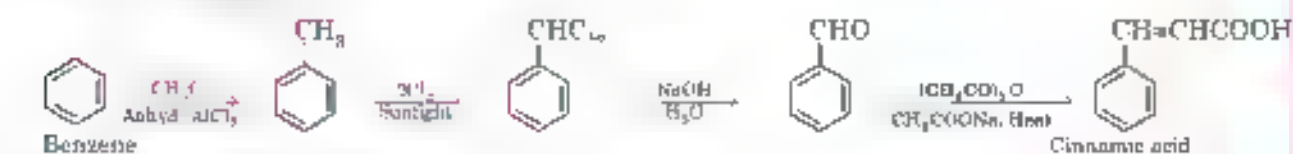
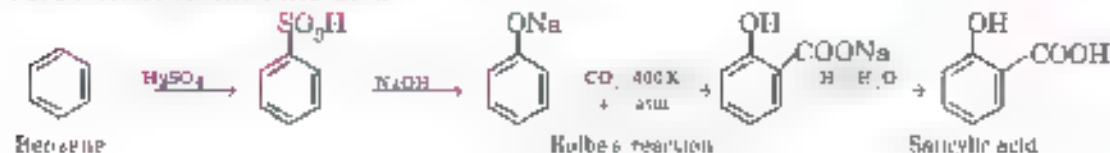


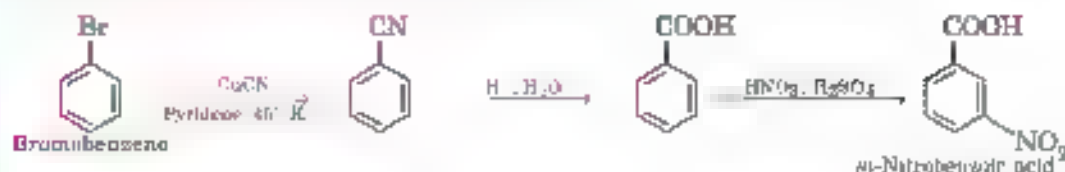
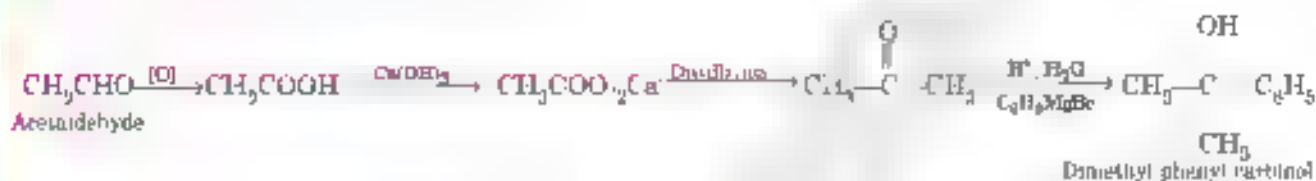
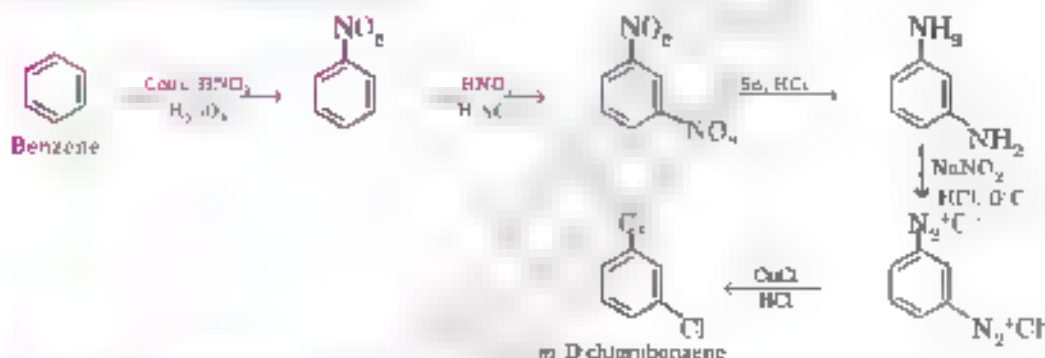
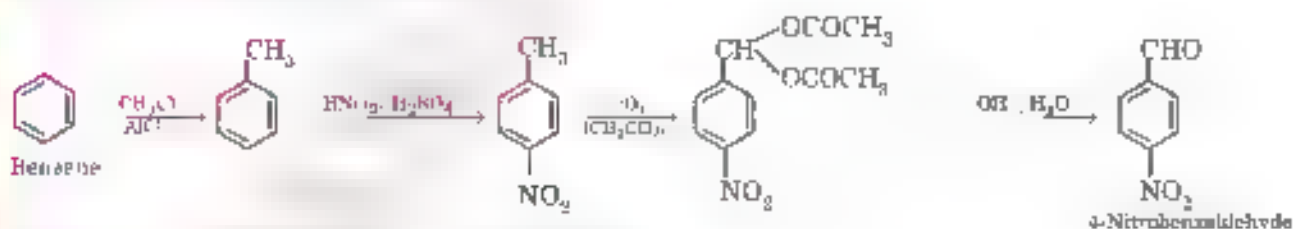
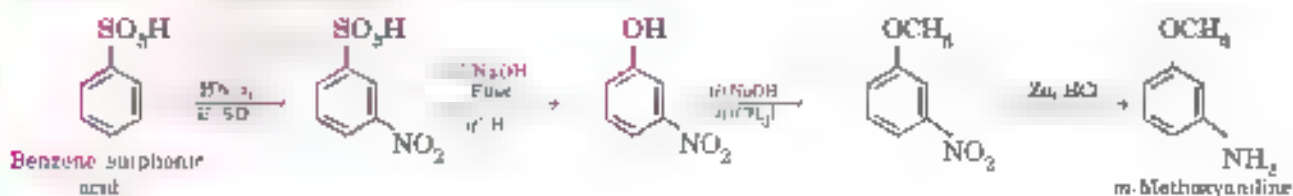
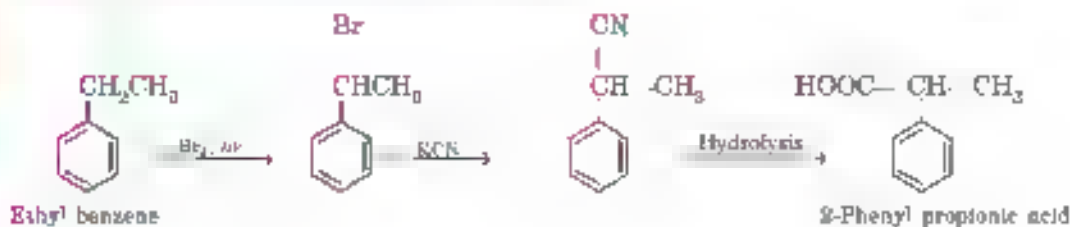
54. Aniline to fluorobenzene



55. Phthalic acid to anthranilic acid



56. Nitrobenzene to anisole**57. Nitrobenzene to benzyl alcohol****58. Benzene sulphonic acid to benzylamine****59. Benzoic acid to aniline****60. Aniline to benzylamine****61. Benzaldehyde to phenyl acetic acid****62. Benzene to cinnamic acid****63. Benzene to salicylic acid**

64. Bromobenzene to m-nitrobenzoic acid**65. Aniline to benzoic acid****66. Acetaldehyde to dimethyl phenyl carbinol****67. Benzene to m-dichlorobenzene****68. Benzene to 4-nitrobenzaldehyde****69. Benzene sulphonic acid to m-methoxyaniline****70. Ethyl benzene to 2-phenyl propanoic acid**

Problems based upon Organic Reactions

2. Compound A ($C_{11}H_{16}O$) reacts rapidly with sodium metal but undergoes no reaction with Lucas reagent at room temperature. It reacts with benzoic acid ($PhSO_3H$) to give B ($C_{17}H_{22}O_2$). Compound B undergoes a reaction with $LiAlH_4$ to give C ($C_{11}H_{18}$). Compound C reacts rapidly with Lucas reagent. What are the compounds A, B, and C?

Ans A = 3-Methylpropan-1-ol B = 2-Methylpropene C = 4-Methylpropan-1-ol

2. A ketone (A) which gives a positive reaction in an oxidation gives a compound (B). The compound on heating with conc. H_2SO_4 gives a compound (C) which forms mono-oxide. The decarboxylation of this mono-oxide gives only acetaldehyde. Identify A, (B) and (C).

Ans. $A = \text{CH}_3\text{COOH}$, $B = \text{CH}_3\text{CH}_2\text{CH}_2\text{COOH}$, $C = \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{COOH}$



3. Compound A (C_6H_6) forms a derivative with benzene-*p*-chloranil with benzene and sodium hydroxide solution. It does not react with Tollen's reagent. What is the structure of A?

Ans. Proton-2-one

4. Compound A ($C_{11}H_{12}O$) on heating with aqueous acid forms a carboxylic acid B and an alcohol C. Compound C with $KMnO_4$ gives B. Write the structures of A, B and C.

Ans. $A = a \int_{-\infty}^{\infty} \delta(x) dx$ properly called R Dirac delta function. It is $\int_{-\infty}^{\infty} \delta(x) dx = 1$ and

5. An optically active amide (A) with molecular formula $C_5H_{11}NO$ on acid hydrolysis gives an acid and ammonia. When A is treated with bromine in acetic acid, it gives a dibromide. On treatment with sodium hydride, it gives an optically active alcohol and nitrogen. The alcohol gives positive iodoform test. What is the structure of A and show the reactions involved?

Ans A is 2-methylbutanamide

6. A compound having molecular formula C_4H_8O forms a crystalline white precipitate with sodium bisulphite and gives a red precipitate with Fehling's solution. Write structural formula, common name, and IUPAC name of the compound. Also give equations for the above reactions.

Ans. $\text{CH}_3\text{CH}_2\text{CHO}$, Propanaldehyde, Propanal

7. Compound A ($C_{11}H_{14}O$) does not give a red precipitate with phenylhydrazine. Oxidation of A with $K_2Cr_2O_7/H^+$ gives B ($C_{11}H_{12}O$). Compound B reacts with phenylhydrazine but does not give Tollen's test. The original compound A can be dehydrated by sulphuric acid to give a hydrocarbon C ($C_{11}H_{10}$). Oxonolysis of the hydrocarbon C gives propene and acetaldehyde. Deduce the structure, formulae of A, B and C.


$$\text{Ans. } \text{A} - \text{H} - \text{CH} - \text{CH} - \text{CH} - \text{CH} - \text{Br} - \text{CH} - \text{CH} - \text{CH} - \text{CH} - \text{HCH}_3$$

- Q 10.** An organic compound A (C_4H_8) is resistant to oxidation by Ferric chloride. Compound B (C_4H_8O) is oxidized with HBr in the presence of PbO_2 to form a compound which reacts with $AgNO_3$ to give $D (C_4H_7Br)$. Give the structures of A, B, C and D along with the reactions.

9. An organic compound (A) C_4H_8O reacts with H_2 giving compound B. H_2 with an oxidising agent gives a normal hydrocarbon having four carbon atoms. On oxidation A gives compound C ($C_4H_8O_2$) and then compound D (C_4H_8O). Deduce the structures of A, B, C and D.

Ана. А) $=C_2H_5OH$; В) $=C_2H_5I$; С) $=C_2H_5CHO$; Д) $=C_2H_5COOH$

- (1) A large, white crystalline solid. A 10% solution with 0.5 g/ml in glacial acetic acid gives a precipitate P and a compound Q. H₂SO₄ drives off Q under acidic conditions, gives L and E. Oxidation of D with KMnO₄ as a reagent gives B. Upon heating with Ca(OH)₂ gives E. Molecular formula of L is C₁₀H₈O. L does not give Tollens' test and does not reduce Fehling solution but forms a 2,4-dinitrophenylhydrazone. Identify A, B, C, D and E.

Ans. A = CH_3COOH B = CH_3COOH C = CH_3COOH D = CH_3COOH

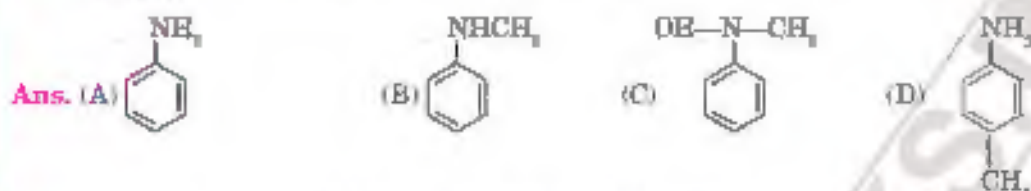
11. Compound A , C_4H_8 , undergoes oxidation to give B , C_4H_6O . B forms a cyclic but does not give Tollen's test. B reacts with aqueous potassium hydroxide to give uniform. Deduce the structures of A and B and show reactions.

Ans. A? Butan-2-ol. (B = 2-butanol)

12. An organic compound (A) on treatment with acetic acid in the presence of sulphuric acid produces an ester (B). (A) on mild oxidation gives (C). (C) with 50% potassium hydroxide followed by acidification with dilute hydrochloric acid generates (A) and (D). (D) when treated with phosphorus pentachloride followed by reaction with ammonia gives (E). (E) on dehydration produces hydrocyanic acid. Identify the compounds A, B, C, D and E.

Ans. (A) CH_3OH (B) $\text{CH}_3\text{COOCH}_3$ (C) HCHO (D) HCOOH (E) HCONH_2

13. An organic compound $\text{C}_7\text{H}_9\text{N}$ (A) on heating with calculated quantity of methyl iodide gives $\text{C}_7\text{H}_9\text{N}$ (B) which reacts with HNO_2 to form $\text{C}_7\text{H}_8\text{N}_2\text{O}$ (C). Hydrochloride of (B) on heating isomerises to another compound (D). Compound (C) on heating with hydrochloric acid regenerates (B). Identify (A), (B), (C) and (D).



14. An organic compound A ($\text{C}_5\text{H}_7\text{N}$) on boiling with alkali gives ammonia and sodium salt of an acid ($\text{C}_5\text{H}_6\text{O}_2$). Upon reduction, A gives C ($\text{C}_5\text{H}_9\text{N}$) which upon treatment with nitrous acid gives D. Deduce the formulae of the compounds A, B, C and D.

Ans. (A) $\text{CH}_3\text{CH}_2\text{CN}$ (B) $\text{CH}_3\text{CH}_2\text{COONa}$ (C) $\text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2$ (D) $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$

15. A compound (A) $\text{C}_6\text{H}_{14}\text{O}$ liberates hydrogen gas with sodium metal. A does not react with sodium hydroxide and gives a positive Lucas test immediately. When A is treated with PBr_3 , compound B is formed ($\text{C}_6\text{H}_{13}\text{Br}$). When B is treated with alcoholic KOH, compound C and D, both having formula C_6H_{12} , are formed. C is a major product while D is a minor product. When C is treated with ozone followed by hydrolysis, only single ketone is formed. The ketone can be shown to be identical with the compound produced by hydration of propyne in the presence of sulphuric acid and Hg^{2+} . Deduce the structural formulae of the compounds A, B, C and D.



16. Compound A ($\text{C}_6\text{H}_{12}\text{O}_2$) on reduction with LiAlH_4 , yielded two compounds (B) and (C). The compound (B) on oxidation gave (D) which upon treatment with aqueous alkali and subsequent heating furnished (E). The latter, on catalytic hydrogenation, gave (C). The compound (D) was oxidised further to give (F) which was found to be monobasic acid (Molecular weight = 90). Deduce the structures of (A), (B), (C), (D) and (E).

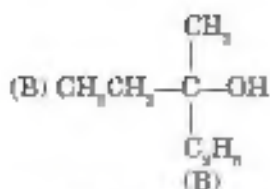
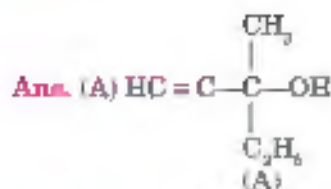
Ans. (A) $\text{CH}_3\text{CH}_2\text{CH}_2\text{COCH}_2\text{CH}_3$ (B) $\text{CH}_3\text{CH}_2\text{OH}$ (C) $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$
(D) CH_3CHO (E) $\text{CH}_3\text{CH}=\text{CHCHO}$

17. Give the structure of (A), (B), (C) and (D)

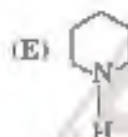
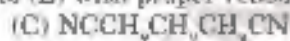
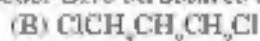
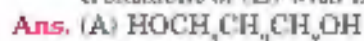
- Compound (A), $\text{C}_4\text{H}_9\text{N}$ reacts with benzene sulphonyl chloride to give a solid insoluble in alkali.
- Compound (B), C_4H_8 which adds on HBr in the presence and absence of peroxide to give the same product.
- Compound (C) C_4H_8 , which when treated with $\text{H}_2\text{SO}_4/\text{H}_2\text{O}$ gives $\text{C}_4\text{H}_{10}\text{O}$ which cannot be resolved into optical isomers.
- Compound D, C_6H_{12} , an optically active hydrocarbon which on catalytic hydrogenation gives an optically inactive compound.

Ans. (A) Ethylmethanamine (B) But-2-ene (C) *trans*-But-2-ene
(D) 3-Methylpent-1-ene.

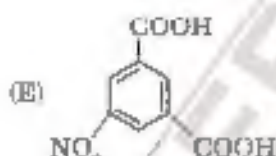
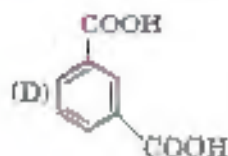
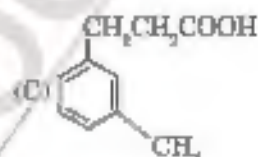
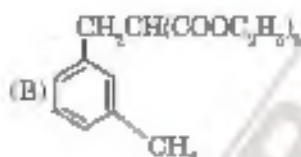
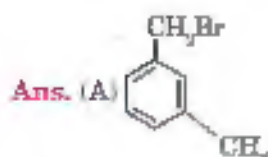
18. An optically active alcohol ($\text{C}_6\text{H}_{12}\text{O}$) absorbs two moles of hydrogen per mole of A upon catalytic hydrogenation and gives a product B. The compound B is resistant to oxidation by CrO_2 and does not show any optical activity. Deduce the structures of A and B.



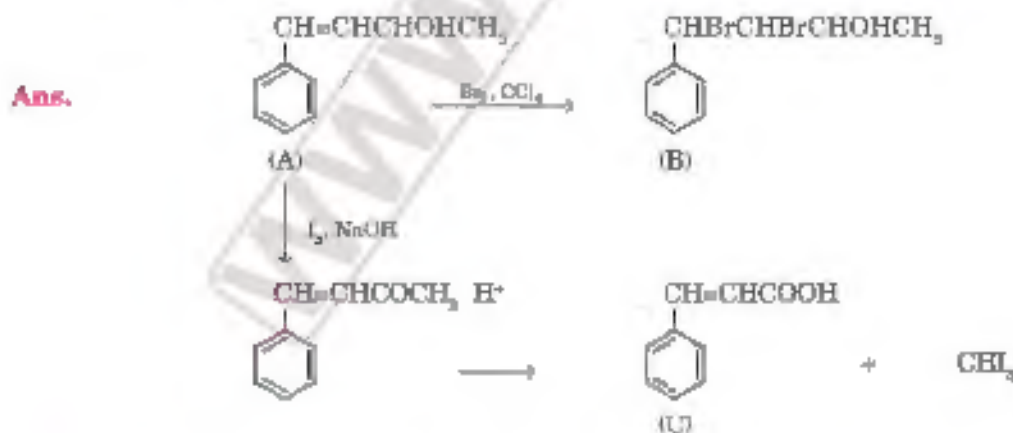
19. An organic compound (A) composed of C, H and O gives characteristic colour with ceric ammonium nitrate. Treatment of (A) with PCl_5 gives (B) which reacts with KCN to form (C). The reduction of (C) with warm $\text{Na/C}_2\text{H}_5\text{OH}$ produces (D) which on heating gives (E) with evolution of ammonia. Pyridine is obtained on treatment of (E) with nitrobenzene. Give structures of (A) to (E) with proper reasoning.



20. An aromatic compound (A), $\text{C}_8\text{H}_9\text{Br}$ reacts with $\text{H}_3\text{C}(\text{COOC}_2\text{H}_5)_2$ in the presence of $\text{C}_2\text{H}_5\text{ONa}$ to give (B). Compound (B) on refluxing with dil H_2SO_4 gives (C) which on vigorous oxidation gives (D). The compound (D) is dibasic but on heating does not give an anhydride. It forms a mononitro derivative (E), in which all the substituents are equidistant from one another. Give structures of (A) to (E) with proper reasoning.



21. Compound (A), $\text{C}_{10}\text{H}_{12}\text{O}$ gives off hydrogen on treatment with sodium metal and also decolourises Br_2 in CCl_4 to give (B), $\text{C}_{10}\text{H}_{12}\text{O} \cdot \text{Br}_2$. (A) on treatment with I_2/NaOH gives iodoform and an acid (C) after acidification. Give structures (A) to (C) and also all the geometrical and optical isomers of (A).



22. An organic acid (A), $\text{C}_8\text{H}_{10}\text{O}_2$ reacts with Br_2 in the presence of phosphorus to give (B). Compound (B) contains an asymmetric carbon atom and yields (C) on dehydro bromination. Compound (C) does not show geometrical isomerism and on decarboxylation gives an alkene (D) which upon ozonolysis gives (E) and (F). Compound (F) gives positive Schiff's test but (E) does not. Give structures of (A) to (F).



Ans. $C_6H_5COCH_3 \xrightarrow[HCl]{NH_3OH} \begin{array}{c} C_6H_5 \\ \diagdown \\ C=N-OH \\ \diagup \\ CH_3 \end{array} \xrightarrow{H^+} CH_3CONHC_6H_5$
 (A) (B) (D)
 $\xrightarrow{HCl} NH_3OH$ $CH_3COCl \xrightarrow{alc. KOH} C_3H_7NH_2$
 (F)
 $\begin{array}{c} C_6H_5 \\ \diagdown \\ C=N-OH \\ \diagup \\ CH_3 \end{array} \xrightarrow{H^+} C_6H_5CONHCH_3 \xrightarrow[OH^-]{alcohol} C_6H_5COOH$
 (C) (E) (G)



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